

F 1503/2

**BULETINUL  
INSTITUTULUI  
POLITEHNIC  
DIN IAȘI**

**Tomul XXXV (XXXIX)**

**Fasc. 1-2**

**Secția II**

**CHIMIE  
ȘI  
INGINERIE CHIMICĂ**

**1989**





# **BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI**



**Tomul XXXV. (XXXIX)**

**Fasc. 1-2**

L: 041641

**Secția II**

**CHIMIE  
ȘI  
INGINERIE CHIMICĂ**

**1989**

### COLEGIUL DE REDACȚIE

Prof. dr. chim. **CAMELUȚA BELDIE** (președinte)  
Prof. dr. ing. **ADRIAN RADU**  
Prof. dr. ing. **M. GAFÎȚANU**  
Conf. dr. ing. **D. LIUȚE**  
Prof. dr. doc. **D. MANGERON**  
Prof. dr. ing. **GH. MAXIM**  
Acad. prof. dr. doc. **CRISTOFOR SIMIONESCU**  
Prof. dr. doc. **GH. CHIRÎȚA**  
Prof. dr. doc. **VALERIU BLIDARU**

*Această fascicolă a apărut și cu sprijinul material al comitetului sindical  
și consiliului U.A.S.C.R. al Institutului politehnic din Iași*

### COMITETUL DE REDACȚIE AL SECȚIEI

#### II. CHIMIE ȘI INGINERIE CHIMICĂ

Prof. dr. doc. **RADU TUDOSE**  
Prof. dr. **ANGELA POPA**  
Prof. dr. ing. **I. ROȘCA**  
Conf. dr. ing. **SPIRIDON OPREA**

### REDACȚIA

Prof. dr. doc. **D. MANGERON**  
(redactor responsabil)  
Prof. dr. ing. **HUGO ROSMAN**  
(secretar)  
Conf. dr. ing. **VICTOR BULACOVSCI**  
(redactor)  
**ECATERINA IRIMIEA**  
(tehnoredactor)



Secția II

CHIMIE ȘI INGINERIE CHIMICĂ

S U M A R

|                                                                                                                                                                                                                | Pag. |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| N. CALU, M. BANGOURA și I. BERDAN, Studiul sistemului de reacție Al(III) — hemateină (franc., rez. rom.) . . . . .                                                                                             | 1    |
| D. BÎLBĂ, N. BÎLBĂ, A. BOLD și I. BERDAN, Separarea ionilor de Al(III), Ga(III), In(III) și Tl(III) pe celuloze fosfat prin cromatografie pe coloană (franc., rez. rom.) . . . . .                             | 7    |
| A. BOLD, A. POPA, M. GĂBURICI, E. POPOVICI și M. CRUCEANU, Site moleculare NaX faze staționare în cromatografia pe strat subțire (III) (engl., rez. rom.) . . . . .                                            | 13   |
| T. ONOFREI, Sorbția și separarea Sr(II) și Ba(II) pe 4(4'-azobenzilceluloza) 1-hidroxi-2-carboxibenzen (engl., rez. rom.) . . . . .                                                                            | 19   |
| A. TARCHON și GH. IONESCU, Eliminarea catalitică a oxigenului din amestecul azot—hidrogen—oxigen utilizat în sinteza amoniacului (engl., rez. rom.) . . . . .                                                  | 23   |
| T. ONOFREI, V. DULMAN, L. ODOCHIAN și V. ȘUNEL, Determinarea gravimetrică a trietilentetraaminei (engl., rez. rom.) . . . . .                                                                                  | 29   |
| <b>I. CURIEVICI</b> , V. NICU, ȘT. UNGUREANU, C. PETRILĂ, R. DIACONESCU, M. NICU, E. IONESCU și S. MATACHE, Modelul matematic al instalației de fabricare a acidului adipic (I) (franc., rez. rom.) . . . . .  | 35   |
| <b>I. CURIEVICI</b> , V. NICU, C. PETRILĂ, ȘT. UNGUREANU, R. DIACONESCU, M. NICU, E. IONESCU și S. MATACHE, Modelul matematic al instalației de fabricare a acidului adipic (II) (franc., rez. rom.) . . . . . | 43   |
| F. MUSTĂȚĂ, R. TUDOSE și E. COSTEA, Studiul experimental al transferului termic la curgerea în filme subțiri de lichide newtoniene (engl., rez. rom.) . . . . .                                                | 53   |
| I. SIMINICEANU, Selectarea și proiectarea compresoarelor pentru industria amoniacului (engl., rez. rom.) . . . . .                                                                                             | 59   |
| C. HAGIU, Îngrășăminte ureo-fosfatice, (engl., rez. rom.) . . . . .                                                                                                                                            | 65   |
| ST. PETRESCU, C. CALISTRU și AL. SZÉP, Cinetica dizolvării KCl în soluție de sulfat de amoniu (engl., rez. rom.) . . . . .                                                                                     | 71   |
| S. IFRIM, C. LUCHIAN și M. BOURCEANU, Determinarea unor caracteristici ale uleiului de tili brut (franc., rez. rom.) . . . . .                                                                                 | 79   |
| AL. CAȘCAVAL, 2-Hidroxicetone (XVIII) (engl., rez. rom.) . . . . .                                                                                                                                             | 85   |
| V. BULACOVȘCHI și M. GROVU-IVĂNOIU, Policondensarea directă a acizilor cicloalcandicarboxilici cu diaminele aromatice în prezența de trifenilfosfit (engl., rez. rom.) . . . . .                               | 89   |
| I. MAZILU, L. TĂTARU, I. COCÎRLĂ, C. PETRESCU și T. LIXANDRU, Contribuții la sinteza, polimerizarea și copolimerizarea unor monomeri vinilici p-substituiți (engl., rez. rom.) . . . . .                       | 95   |



Section II

CHEMISTRY AND CHEMICAL ENGINEERING

C O N T E N T S

|                                                                                                                                                                                                                                              | Pp. |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| N. CALU, M. BANGOURA et I. BERDAN, Étude du système de réaction Al(III) — hemateïne (French, Romanian summary) . . . . .                                                                                                                     | 1   |
| D. BÎLBĂ, N. BÎLBĂ, A. BOLD et I. BERDAN, Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur des celluloses phosphate par chromatographie sur colonne (French, Romanian summary) . . . . .                                         | 7   |
| A. BOLD, A. POPA, M. GĂBURICI, E. POPOVICI and M. CRUCEANU, Molecular Sieves NaX as Stationary Phases for Thin Layer Chromatography (III), (English, Romanian summary) . . . . .                                                             | 13  |
| T. ONOFREI, Sr(II) and Ba(II) Sorption and Separation on 4(4'-Azobenzylcel-<br>lulose) 1-hydroxy-2-carboxybenzene (English, Romanian summary) . . . .                                                                                        | 19  |
| A. TARHON and GH. IONESCU, Catalytic Removal of Oxygen from the Nitro-<br>gen — Hydrogen — Oxygen Mixture Used in the Ammonia Synthesis<br>(English, Romanian summary) . . . . .                                                             | 23  |
| T. ONOFREI, V. DULMAN, L. ODOCHIAN and V. ȘUNEL, Gravimetric Deter-<br>mination of Triethylenetetramine (English, Romanian summary), . . . .                                                                                                 | 29  |
| <b>I. CURIEVICI</b> , V. NICU, ȘT. UNGUREANU, C. PETRILĂ, R. DIACONESCU,<br>M. NICU, E. IONESCU et S. MATACHE, Le modèle mathématique de<br>l'installation de fabrication de l'acide adipique (I) (French, Romanian<br>summary) . . . . .    | 35  |
| <b>I. CURIEVICI</b> , V. NICU, C. PETRILĂ, ȘT. UNGUREANU, R. DIACONESCU,<br>M. NICU, E. IONESCU et S. MATACHE, Le modèle mathématique de<br>l'installation de fabrication de l'acide adipique (II) (French, Romanian sum-<br>mary) . . . . . | 43  |
| F. MUSTĂȚĂ, R. TUDOSE and E. COSTEA, Experimental Study on Meat Trans-<br>fer in Thin Films of Non-newtonian Liquids (English, Romanian sum-<br>mary) . . . . .                                                                              | 53  |
| I. SIMINICEANU, Selection and Design of the Compressors for Ammonia Indus-<br>try (English, Romanian summary) . . . . .                                                                                                                      | 59  |
| C. HAGIU, Urea-Ammonium Phosphates Fertilisers (English, Romanian sum-<br>mary) . . . . .                                                                                                                                                    | 65  |
| ST. PETRESCU, C. CALISTRU and AL. SZÉP Kinetics of KCl Dissolving<br>in Ammonium Suphate Solution (English, Romanian summary) . . . . .                                                                                                      | 71  |
| S. IFRIM, C. LUCHIAN et M. BOURCEANU, Détermination de quelques carac-<br>téristiques du talloil brut (French, Romanian summary) . . . . .                                                                                                   | 79  |
| AL. CAȘCAVAL, 2-Hydroxyketones (XVIII) (English, Romanian summary) .                                                                                                                                                                         | 85  |
| V. BULACOVACHI and M. GROVU-IVĂNOIU, Direct Polycondensation of<br>Cycloaliphatic Dicarboxylic Acids with Diamines Catalysed by Triphenyl<br>Phosphite (English, Romanian summary) . . . . .                                                 | 89  |
| I. MAZILU, L. TĂTARU, I. COCÎRLĂ, C. PETRESCU and T. LIXANDRU,<br>Contributions to the Synthesis, Polymerization and Copolymerization of<br>some p-Substituted Vinylic Monomers (English, Romanian summary) .                                | 95  |



Секция II

ХИМИА И ХИМИЧЕСКАЯ ПРОМЫШЛЕННОСТЬ

СО Д Е Р Ж А Н И Е

|                                                                                                                                                                                                                  | Стр. |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Н. КАЛУ, М. БАНГУРА и И. БЕРДАН, Изучение реакционной система Al (III)—гематоин (франц., рез. рум.) . . . . .                                                                                                    | 1    |
| Д. БЫЛБЭ, Н. БЫЛБЭ, А. БОЛД и И. БЕРДАН, Сепарация ионов Al (III), Ga (III), In (III) и Tl (III) на фосфатных целлюлоз в холонновой хроматографии (франц., рез. рум.) . . . . .                                  | 7    |
| А. БОЛД, А. ПОПА, М. ГЭБУРИЧ, Е. ПОПОВИЧ и М. КРУЧЯНУ, Молекулярные сита для тонкослойной хроматографии. Расделение органических красителей (англ., рез. рум.) . . . . .                                         | 13   |
| Т. ОНОФРЕЙ, Сорбция и отделения Sr (II) и Ba (II) на 4 (4'-азобензилцеллюлозе) 1-гидрокси-2- карбоксибензене (англ., рез. рум.) . . . . .                                                                        | 19   |
| А. ТАРХОН и Г. ИОНЕСКУ, Каталитическое устранение кислорода из N <sub>2</sub> —H <sub>2</sub> смеси употребляющий в синтезе аммиака (англ., рез. рум.) . . . . .                                                 | 23   |
| Т. ОНОФРЕЙ, В. ДУЛМАН, Л. ОДОКЯН и В. ШУНЕЛ, Гравиметрическое определение триэтилентетрамина (англ., рез. рум.) . . . . .                                                                                        | 29   |
| <u>И. КУРЬЕВИЧ</u> , В. НИКУ, ШТ. УНГУРЯНУ, К. ПЕТРИЛЭ, Р. ДИАКОНЕСКУ, М. НИКУ, Е. ИОНЕСКУ и С. МАТАКЕ, Математический модель для установки для фабрикации адипинового кислота (I) (франц., рез. рум.) . . . . . | 35   |
| <u>И. КУРЬЕВИЧ</u> , В. НИКУ, С. ПЕТРИЛЭ, ШТ. УНГУРЯНУ, Р. ДИАКОНЕСКУ, М. НИКУ, Е. ИОНЕСКУ и С. МАТАКЕ, Математический модель для фабрикации адипинового кислота (II) (франц., рез. рум.) . . . . .              | 43   |
| О. МУСТАЦЭ, Р. ТУДОСЕ и Е. КОСТЯ, Экспериментальное изучение переноса теплоты в тонких пленок (англ., рез. рум.) . . . . .                                                                                       | 53   |
| И. СИМИНИЧЯНУ, Выборка и проэктирование компрессоров для производства аммиака (англ., рез. рум.) . . . . .                                                                                                       | 59   |
| К. ХАДХИУ, Карбоамофос (англ., рез. рум.) . . . . .                                                                                                                                                              | 65   |
| С. ПЕТРЕСКУ, К. КАЛИСТРУ и А. СЕП, Растворение KCl в растворе сульфата аммония (англ., рез. рум.) . . . . .                                                                                                      | 71   |
| С. ИФРИМ, К. ЛУКЯН и М. БОУРЧЯНУ, Определение некоторых характеристик таллового масла (франц., рез. рум.) . . . . .                                                                                              | 79   |
| АЛ. КАШКАВАЛ, 2-гидроксикетоны (XVIII) (англ., рез. рум.) . . . . .                                                                                                                                              | 85   |
| В. БУЛАКОВСКИЙ и М. ГРОВУ-ИВЭНОЮ, Прямая поликонденсация циклоалифатических дикарбоновых кислот с диаминами в присутствии трифенилфосфита (англ., рез. рум.) . . . . .                                           | 89   |
| И. МАЗИЛУ, Л. ТЭТАРУ, И. КОКЫРЛЭ, К. ПЕТРЕСКУ и Т. ЛИСКАНДРУ, Вклад в синтезе, полимеризации и сополимеризации некоторых виниловых р-замещенных мономеров (англ., рез. рум.) . . . . .                           | 95   |





## ÉTUDE DU SYSTÈME DE RÉACTION Al(III)—HEMATÉINE

PAR

N. CALU, M. BANGOURA et I. BERDAN

### 1. Introduction

Dans la réaction entre l'ion Al(III) et l'hématéine se forment, successivement, des complexes solubles. En général, l'évolution de ce système de réaction s'accorde avec le principe de la compatibilité des acides Lewis avec les bases Lewis, à savoir, les acides de classe  $a$  ( $Al^{3+}$ ,  $Ti^{4+}$ , etc.) préfèrent à la coordination les ligands contenant des atomes fortement électronégatifs tel que l'atome d'oxygène de la molécule d'hématéine [1]...[3].

Bien que la formation des complexes dans le système mentionné ci-dessus est utilisée dans des buts analytiques [4], on ne trouve pas dans la littérature des recherches complètes, approfondies, sur la stabilité et la structure des espèces formées. En ce sens, le présent travail apporte de nouvelles informations concernant le processus de coordination de l'hématéine à l'ion Al(III).

### 2. Partie expérimentale

Les processus de formation des complexes entre l'ion Al(III) et l'hématéine ont été étudiés en milieu d'eau — alcool éthylique, dans des rapports qui varient entre 4 : 1 et 1 : 1,5. Les conditions de réaction ont été les suivantes :

$AlCl_3$  :  $c = 1 \cdot 10^{-4} \dots 2 \cdot 10^{-3}$  moles/l ;

Hématéine :  $c = 1 \cdot 10^{-4} \dots 2 \cdot 10^{-3}$  moles/l ;

Solution tampon :  $CH_3COOH-NaCH_3COO$ , ayant des valeurs du pH différentes.

Les processus de formation des complexes ont été suivis par voie spectroscopique, les mesures d'absorbance étant effectuées à l'aide d'un spectrophotomètre de type SPEKORD UV—VIS, Carl Zeiss—Jena. Pour les mesures de pH on a utilisé un pH-mètre PHM—Radiometer Copenhague.

### 3. Résultats et discussions

#### 3.1. Le caractère acido-basique de l'hématéine

Le caractère acido-basique de l'hématéine a été investigué par titrages pH-métriques avec une solution de KOH, dans des systèmes de concentrations différentes (Fig. 1 et 2) :

Sur les courbes de titrage pH-métrique de l'hématéine on met en évidence la neutralisation de celle-ci, qui correspond à l'ionisation successive de deux protons.

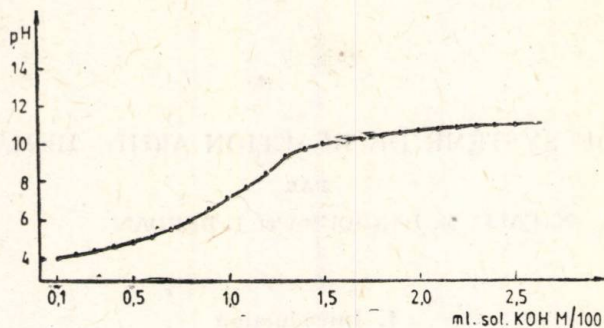


Fig. 1. — Titrage pH-métrique de l'hématéine avec KOH, en milieu eau-alcool éthylique, 4:1. Hématéine — 5 ml de concentration  $2 \cdot 10^{-3}$  moles/l ; KOH —  $2 \cdot 10^{-2}$  moles/l ;  $t = 18^\circ\text{C}$ .

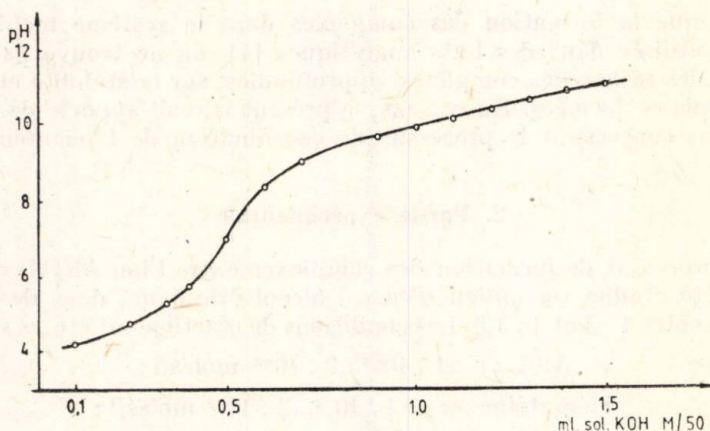


Fig. 2. — Titrage pH-métrique de l'hématéine avec KOH, en milieu eau-alcool éthylique, 4:1. Hématéine — 5 ml de concentration  $1 \cdot 10^{-3}$  moles/l ; KOH —  $1 \cdot 10^{-2}$  moles/l ;  $t = 18^\circ\text{C}$ .

Les constantes d'acidité de l'hématéine, calculées à partir des déterminations pH-métriques, ont les valeurs :

$$\text{pK}_{a1} = 4,99 \text{ et } \text{pK}_{a2} = 5,31.$$

### 3.2 La formation de complexes dans le système Al(III) — hématéine

La formation de complexes dans le système Al (III) — hématéine a été étudiée par voie spectrophotométrique.

L'hématéine libre présente, dans le domaine visible du spectre électronique, une bande d'absorption avec  $\lambda_{\text{max}} = 22\,300 \text{ cm}^{-1}$ . À la suite de sa coor-



dination avec l'ion  $\text{Al(III)}$ , dans le spectre apparait un effet bathochrome dont la grandeur dépend de la composition du milieu de réaction. La bande à transfert de charge, caractéristique du complexe formé, située à  $\lambda_{\text{max}} = 19680 \text{ cm}^{-1}$ , est proportionnelle à la concentration du complexe (Fig. 3).

a) *La composition des complexes du système  $\text{Al(III)}$ —hématine*

Dans la réaction entre l'ion  $\text{Al}_{\text{aq}}^{3+}$  ( $M$ ) et l'hématine ( $L$ ), les complexes se forment successivement. Pour la détermination de leur composition on a utilisé des méthodes spectrophotométriques, en effectuant les mesures d'absorbance sur des solutions stabilisées dans le temps. Les solutions de réactants ont été préparées avec et sans système tampon.

Dans le cadre de la méthode des rapports molaires [5] on a effectué les déterminations expérimentales d'absorbance ( $A$ ) tant pour  $[M] = \text{const.}$  que pour  $[L] = \text{const.}$  Les représentations graphiques des fonctions  $A = f(L/M)$  et  $A = f(M/L)$  sont données dans les Fig. 4 et 5. Les données ainsi obtenues mettent en évidence les étapes suivantes de réaction :

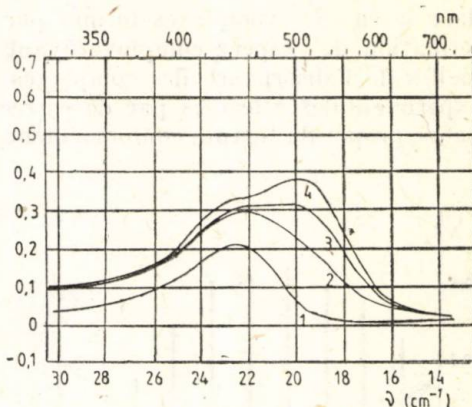


Fig. 3. — Spectres d'absorption enregistrés sur les solutions d'hématine et de ses complexes avec  $\text{Al(III)}$ , en milieu eau—alcool éthylique 2,33 : 1. Temps de réaction — 24 heures, cuve—0,2 cm ; 1 — Hématine—  $3 \cdot 10^{-4}$  moles/l ; 2 —  $1 \cdot 10^{-4}$  moles/l  $\text{AlCl}_3$  —  $3 \cdot 10^{-4}$  moles/l hématine (1 M : 3 L) ; 3 —  $2 \cdot 10^{-4}$  moles/l  $\text{AlCl}_3$  —  $3 \cdot 10^{-4}$  moles/l hématine (1 M : 1,5 L) ; 4 —  $3 \cdot 10^{-4}$  moles/l  $\text{AlCl}_3$  —  $3 \cdot 10^{-4}$  moles/l hématine (1 M : 1 L).

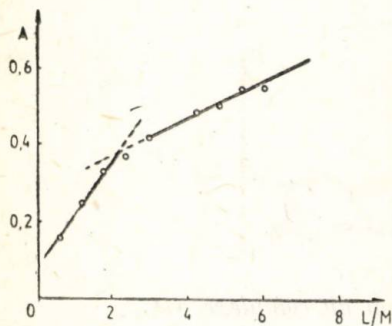


Fig. 4. — Représentation graphique de la fonction  $A = f(L/M)$ , pour le système  $\text{Al(III)}$  — hématine, en milieu eau — alcool éthylique ;  $[M] = 2 \cdot 10^{-4}$  moles/l ;  $\lambda = 19000 \text{ cm}^{-1}$  ; cuve—0,1 cm.

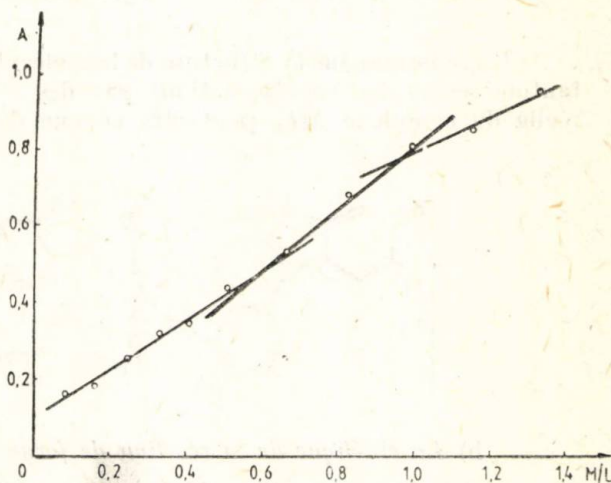
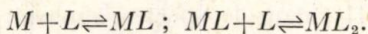


Fig. 5. — Représentation graphique de la fonction  $A = f(M/L)$ , pour le système  $\text{Al(III)}$  — hématine, en milieu eau — alcool éthylique, 4,55 : 1 :  $[L] = 3,6 \cdot 10^{-4}$  moles/l. Tampon :  $\text{CH}_3\text{COOH}$  —  $\text{NaCH}_3\text{COO}$  (pH=4) ; temps de réaction — 2 heures ;  $\lambda = 19350 \text{ cm}^{-1}$  ; cuve — 0,2 cm.





Dans le cadre de la méthode des variations continues [6], peu utilisée dans le cas des complexes formés par étapes, on observe, en particulier, la formation de l'espèce complexe ayant un rapport molaire 1:1. Les valeurs réelles de l'absorbance des complexes ont été obtenues à partir des valeurs expérimentales affectées par de corrections qui tiennent compte de l'absorbance propre du ligand, conformément au procédé de la Fig. 6 *a* et 6 *b*.

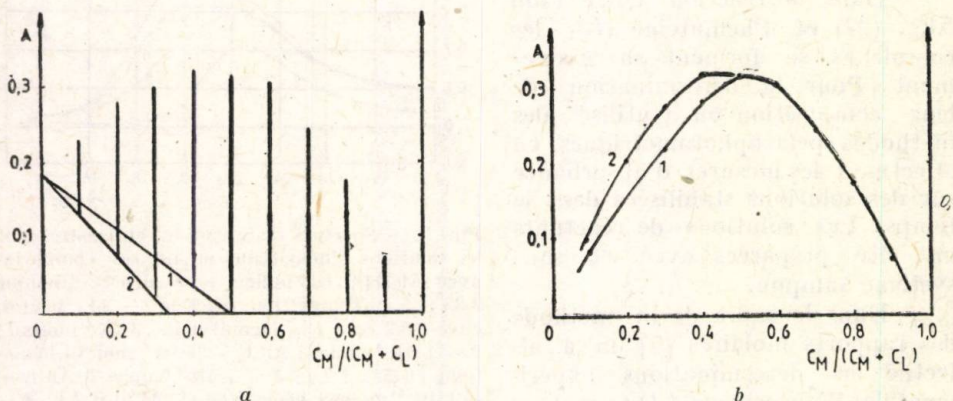
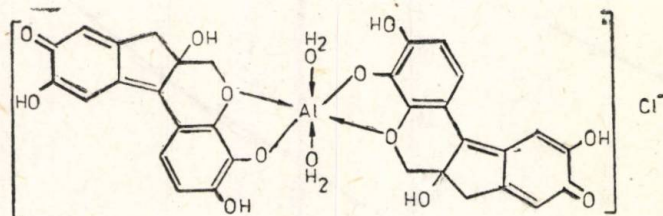


Fig. 6. — Représentation graphique de la fonction  $A = f[C_M / (C_M + C_L)]$ , pour le système Al(III) — hématine :  $C_M / (C_M + C_L) = 1$ ;  $AlCl_3 - 4 \cdot 10^{-4}$  moles/l;  $C_M / (C_M + C_L) = 0$ ; Hématine —  $4 \cdot 10^{-4}$  moles/l. Temps de réaction — 100 min.;  $\lambda = 19\,350\text{ cm}^{-1}$ ; cuve — 0,2 cm; *a* — élimination de l'absorbance du ligand des valeurs expérimentales, suivant les droites 1 (ML) et 2 ( $ML_2$ ); *b* — la fonction  $A = f[C_M / (C_M + C_L)]$  avec les valeurs corrigées.

En se basant sur la structure de la molécule d'hématine, avec ses formes tautomères et les représentations par des structures limites, la structure réelle du complexe  $ML_2$  peut être conçue de la forme :



#### b) La cinétique de la réaction de formation du complexe $ML_2$

La réaction entre l'ion  $Al^{3+}_{aq}$  et l'hématine se produit dans un certain intervalle de temps et est influencée par le pH du milieu de réaction.

Les calculs effectués à partir des mesures spectrophotométriques montrent que la réaction de formation des complexes commence suivant une ciné-



tique d'ordre 1, par rapport au métal, qui change dans le temps, avec une constante de vitesse qui dépend du pH de la solution (Tableau 1).

Tableau 1

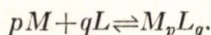
Variation de la constante de vitesse en fonction du pH de la solution au cours de la formation des complexes dans le système Al(III) — hémateïne

| No. | pH  | Constante de vitesse<br>$k \cdot 10^2 \text{ min.}^{-1}$ |
|-----|-----|----------------------------------------------------------|
| 1   | 3,8 | 5,7                                                      |
| 2   | 4,0 | 5,2                                                      |
| 3   | 4,5 | 5,0                                                      |
| 4   | 5,0 | 4,6                                                      |
| 5   | 5,5 | 5,2                                                      |
| 6   | 6,0 | 5,5                                                      |

La diminution de la vitesse de réaction dans l'intervalle de pH = 3,8...5,0 peut être corrélée avec l'état dissout du générateur de complexe qui passe dans des formes partiellement basiques, moins réactives, alors que son augmentation, à des pH plus élevés, est liée au processus prépondérant de déprotonation du ligand.

c) La stabilité du complexe  $ML_2$

La stabilité du complexe  $ML_2$  est appréciée à l'aide de la constante globale de stabilité,  $\beta_2$ , déterminée par mesures spectrophotométriques, propre à l'équation d'équilibre :



Ainsi, par application de la méthode Bent—French [7], en se basant sur la relation :

$$\log \beta_n = \log [M_pL_q] - p \log [M] - q \log [L],$$

on a obtenu la valeur

$$\beta_2 = 3,18 \cdot 10^8 \text{ l}^2 \cdot \text{moles}^{-2}.$$

En utilisant la méthode Edmonds—Birnbau m [8], partant de la relation :

$$\beta_n = (C_L^n \cdot A'' - C_{L'}^n \cdot A') / [C_L^n \cdot C_{L'}^n \cdot (A' - A'')]$$

on a obtenu les données indiquées dans le Tableau 2.

La valeur de la constante globale de stabilité, calculée par cette voie, est  $\beta_2 = 0,47 \cdot 10^8 \text{ l}^2 \cdot \text{moles}^{-2}$ . La constante globale moyenne,  $\bar{\beta}_2 = 1,82 \cdot 10^8 \text{ l}^2 \cdot \text{moles}^{-2}$ , indique une bonne stabilité pour le complexe  $ML_2$  du système Al(III)—hémateïne.



Tableau 2

Données concernant la stabilité du complexe  $ML_2$  du système  $Al(III)$ —hémateïne obtenues par la méthode Edmonds—Birnbaurn

| Paire de solutions | $C_M$<br>moles/l    | $C_L$<br>moles/l                           | Absorbance<br>A | $\beta_n$<br>$l^n \cdot \text{moles}^{-n}$ |                   |                      |
|--------------------|---------------------|--------------------------------------------|-----------------|--------------------------------------------|-------------------|----------------------|
|                    |                     |                                            |                 | n=1                                        | n=2               | n=3                  |
| 1<br>2             | $0,2 \cdot 10^{-3}$ | $1,6 \cdot 10^{-4}$<br>$2,4 \cdot 10^{-4}$ | 0,35<br>0,47    | $0,19 \cdot 10^4$                          | $0,45 \cdot 10^8$ | $0,42 \cdot 10^{12}$ |
| 1<br>3             | $0,2 \cdot 10^{-3}$ | $1,6 \cdot 10^{-4}$<br>$3,2 \cdot 10^{-4}$ | 0,35<br>0,53    | $0,29 \cdot 10^4$                          | $0,47 \cdot 10^8$ | $0,38 \cdot 10^{12}$ |
| 2<br>3             | $0,2 \cdot 10^{-3}$ | $2,4 \cdot 10^{-4}$<br>$3,2 \cdot 10^{-4}$ | 0,47<br>0,53    | $0,50 \cdot 10^4$                          | $0,49 \cdot 10^8$ | $0,29 \cdot 10^{12}$ |

#### 4. Conclusions

L'ion  $Al_{aq}^{3+}$  forme, successivement, avec l'hémateïne, des complexes de type  $ML$  et  $ML_2$ . Le processus de formation des complexes a lieu suivant une cinétique d'ordre 1, par rapport au métal, qui change dans le temps, avec une constante de vitesse qui dépend du pH de la solution.

Les deux premières constantes d'acidité de l'hémateïne sont :  $pK_{a1} = 4,99$  et  $pK_{a2} = 5,31$ .

Dans la structure des complexes  $ML$  et  $ML_2$  se trouvent des cycles spécifiques aux complexes internes.

La constante globale de stabilité du complexe  $ML_2$ , calculée à partir des données spectrophotométriques, est  $\beta_2 = 1,82 \cdot 10^8 l^2 \cdot \text{moles}^{-2}$ .

Reçue le 13 février 1987

Institut Polytechnique, Jassy,  
Chaire de Chimie Anorganique  
Analytique  
et Faculté d'Agronomie,  
et  
Jolo-Mamou, Guinée

#### B I B L I O G R A P H I E

1. Ahrland S., *Structure and Bonding*. Vol. 1, Springer-Verlag, Berlin, Heidelberg, New-York, 1966.
2. Ahrland S., Chatter J., Davies N. R., *Quart. Rev.*, **12**, 265 (1958).
3. Pearson R., *J. Amer. Chem. Soc.*, **85**, 3533 (1963).
4. Singhal G. K., Taudon K. H., *Talanta*, **15**, 7, 707 (1968).
5. Yoe G., Jones A., *Ind. Eng. Chem. Analyt. Ed.*, **16**, 11 (1944).
6. Job P., *Ann. Chim. (France)*, **9**, 113 (1928); *Ibid.*, **6**, 97 (1936).
7. Bent H. E., French C. L., *J. Amer. Chem. Soc.*, **63**, 568 (1941).
8. Edmonds S. M., Birnbaum N., *J. Amer. Chem. Soc.*, **63**, 1471 (1941).

#### STUDIUL SISTEMULUI DE REACȚIE $Al(III)$ — HEMATEINĂ

(Rezumat)

Ionul  $Al_{aq}^{3+}$  formează cu hemateina combinații complexe solubile. Reacția de complexare se desfășoară în timp, corespunzător unei cinetici de ordinul 1, cu constanta de viteză depinzând de mediul de reacție; la pH = 5, valoarea constantei de viteză este  $k = 4,6 \cdot 10^{-2} \text{ min}^{-1}$ .

Compoziția complexilor, determinată prin metode spectrofotometrice, corespunde formulelor generale  $ML$  și  $ML_2$  ( $M=Al$  și  $L$  = hemateină). În structura moleculară a complexilor se formează cicluri specifice complexilor interni. Constanta globală de formare a complexului  $ML_2$  este  $\beta_2 = 1,82 \cdot 10^8 l^2 \cdot \text{mol}^{-2}$ . Primele două constante de aciditate ale hemateinei sînt :  $pK_{a1} = 4,99$  și  $pK_{a2} = 5,31$ .



## SÉPARATION DES IONS $Al(III)$ , $Ga(III)$ , $In(III)$ ET $Tl(III)$ SUR DES CELLULOSES PHOSPHATE PAR CHROMATOGRAPHIE SUR COLONNE

PAR

DOINA BÎLBĂ, N. BÎLBĂ, ANIȘOARA BOLD et I. BERDAN

### 1. Introduction

La séparation de l'aluminium, du gallium, de l'indium et du thallium présente une grande importance tant au point de vue pratique — grâce à leur utilisation assez fréquente dans la technique moderne, qu'analytique — compte tenu que leurs propriétés physico-chimiques et de leurs combinaisons sont semblables.

La séparation complète des ions  $Al(III)$ ,  $Ga(III)$ ,  $In(III)$  et  $Tl(III)$  par échange ionique sur colonne a été effectuée pour la première fois par K r a u s et collaborateurs, en utilisant de la résine anionique Dowex-1 ( $Cl^-$ ), en réalisant l'élution des éléments avec des solutions aqueuses d'acide chlorhydrique en fonction de la stabilité des chlorocomplexes formés [1].

Par voie expérimentale on constate que l'addition des solvants organiques à la solution chlorhydrique modifie le mécanisme de formation des chlorocomplexes et par conséquent les facteurs de séparation [2] ... [5]. Ainsi, en utilisant comme éluants les mélanges : acide chlorhydrique — alcools aliphatiques inférieurs, acide chlorhydrique — acétone, on a réalisé la séparation quantitative de l'aluminium, du gallium, de l'indium et du thallium sur des résines anioniques [6] et cationiques [7]...[9].

On mentionne toutefois que la séparation de ces éléments a été effectuée aussi bien et par chromatographie en couche mince sur des celluloses non-modifiées, en réalisant l'élution avec des mélanges acides halogénés — alcools [10] ou acides halogénés — acétone [11].

Dans ce qui suit on présente les résultats obtenus concernant la séparation de l'aluminium, du gallium, de l'indium et du thallium sur des celluloses phosphate, par chromatographie sur colonne.

### 2. Partie expérimentale

On a opéré avec des solutions de chlorures d'aluminium, de gallium, d'indium et de thallium (produits p.a.) standardisées, en utilisant des méthodes gravimétriques. Comme échangeurs d'ions on a utilisé deux sortes de cellulose phosphate dont les caractéristiques sont présentées dans le Tableau 1.

Les déterminations ont été effectuées tant dans des conditions statiques que dynamiques.

En conditions statiques, des échantillons pesant environ 0,5 g cellulose phosphate sont mis en contact avec 25 ml solution qui contient l'ion à échanger



(~1 mg) et des quantités variables d'acide chlorhydrique et de solvant organique. Après 24 heures, sous agitation intermittente, on sépare les phases et on détermine le contenu en ions de la solution par des méthodes spectrophotométriques appropriées.

Tableau 1

*Propriétés caractéristiques des celluloses — échangeurs d'ions*

| Cellulose ionitique      | Groupe ment échangeur d'ions      | pK <sub>a</sub> | Capacité d'échange m.éq./g | Valeur du pH pour la capacité maximum |     |
|--------------------------|-----------------------------------|-----------------|----------------------------|---------------------------------------|-----|
| P <sub>10</sub> -Serva   | —O—PO <sub>3</sub> H <sub>2</sub> | 6,6             | 0,74                       | 1H                                    | 1,5 |
| P <sub>11</sub> -Whatman | —O—PO <sub>3</sub> H <sub>2</sub> | 6,5             | 2,60                       | 1H                                    | 1,5 |
|                          |                                   | 9,5             | 4,20                       | 2H                                    | 7,5 |

On exprime quantitativement la distribution d'ions à l'équilibre par l'intermédiaire du coefficient de distribution  $K_d$ .

La séparation est effectuée en faisant passer des mélanges qui contiennent ~1 mg de chaque élément, par la colonne de cellulose ionitique imprégnée, préalablement, avec un éluant adéquat. L'éluant est ramassé à l'aide d'un collecteur automatique de fractions sous une vitesse d'écoulement de 0,5...1 ml/min. Après l'enlèvement du solvant par évaporation, chaque essai est soumis à l'analyse qualitative et quantitative.

### 3. Résultats et discussions

Les déterminations effectuées dans des conditions statiques ont mis en évidence l'influence de l'acidité du milieu et des solvants organiques (nature, concentration) sur la sorption des ions Al(III), Ga(III), In(III) et Tl(III) sur des celluloses phosphate [12], [13].

Les données expérimentales montrent que l'augmentation de la concentration de HCl dans la solution aqueuse, à l'équilibre, produit une diminution considérable de la sorption des ions et, par suite, les valeurs des coefficients de distribution peuvent être corrélées avec la capacité des ions de former des chlorocomplexes.

L'influence des solvants organiques sur la sorption des ions est due à la nature de ceux-ci (structure, constante diélectrique) et à leur concentration dans la solution initiale.

D'une manière générale, pour des fortes concentrations en HCl et solvant organique, les coefficients de distribution s'écartent sensiblement par rapport aux valeurs qui correspondent aux systèmes aqueuses.

Les résultats obtenus nous a permis de sélectionner les meilleures conditions, pour séparer les éléments mentionnés ci-dessus.



### 3.1. Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur la cellulose $P_w$ -Serva

Pour séparer les éléments sur la cellulose phosphate  $P_w$ -Serva on a utilisé comme éluants les mélanges suivants : HCl 0,01 M (20%) — méthanol (80%) et HCl 0,5 M (40%) — éthanole (60%).

Les valeurs des coefficients de distribution des ions Al(III), Ga(III), In(III) et Tl(III) sur la cellulose  $P_w$  dans le mélange HCl 0,01 M — méthanol (80%) sont présentées dans la Fig. 1. On observe que les différences entre les coefficients de distribution augmentent, les facteurs de séparation sont plus élevés et, par conséquent, la séparation s'améliore.

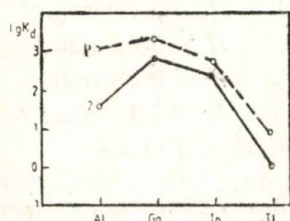


Fig. 1. — Distribution des ions Al(III), Ga(III), In(III), Tl(III) sur cellulose phosphate  $P_w$ -Serva: 1 — solution aqueuse HCl 0,01 M; 2 — mélange 20% HCl 0,01 M — 80% alcool méthylique.

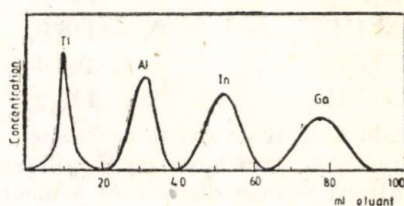


Fig. 2. — Séparation des ions Al(III), Ga(III), In(III), Tl(III) sur cellulose phosphate  $P_w$ -Serva avec l'éluant : 20% HCl 0,01 M — 80% alcool méthylique.

La séparation suggérée a été pratiquement vérifiée en passant un mélange synthétique qui contient ~1 mg de chacun des éléments sur une colonne avec  $\varnothing = 10$  mm remplie avec 9 g cellulose  $P_w$ -Serva, la longueur du lit de sorbent étant égale à 750 mm.

Le mélange à séparer a été élué avec un volume total de 90 ml de mélange HCl 0,01 M — méthanol (80%). Les ions sont desorbés suivant l'ordre :

$$Tl(III) > Al(III) > In(III) > Ga(III).$$

La courbe expérimentale d'éluion est représentée dans la Fig 2.

Pour apprécier l'efficacité de séparation de la colonne chromatographique on a calculé le nombre de plateaux théoriques,  $N$ , ainsi que l'hauteur équivalente du plateau théorique,  $H$ .

Conformément à la théorie des plateaux, le nombre de passages effectives sorption — desorption ou le nombre de plateaux théoriques,  $N$ , on peut le calculer à l'aide de la relation :

$$N = 16 \left( \frac{V_{\max}}{w} \right)^2 = 8 \left( \frac{V_{\max}}{\beta} \right)^2 = \left( \frac{V_{\max}}{\sigma} \right)^2,$$

où:  $V_{\max}$  représente le volume de rétention, [ml], (volume d'éluant qui correspond à la concentration maximum de l'ion desorbé);  $w$  — largeur de la bande d'éluion, à la base de la curve Gauss, mesurée entre les tangentes aux points d'inflexion, [ml];  $\sigma$  — écartement standard en tant que mesure de la



dispersion de la zone ( $w = 4\sigma$ );  $\beta$  — largeur du pic chromatographique (de la bande d'élution) mesurée à l'hauteur de l'ordonnée :

$$C = \frac{C_{\max}}{e} = 0,368 C_{\max}, \quad \beta = 2\sqrt{2}\sigma.$$

L'efficacité de la colonne chromatographique dépend de la hauteur du plateau théorique,  $H = L/N$ , où :  $L$  — longueur du lit de sorbent de la colonne, [mm];  $N$  — nombre de plateaux théoriques.

En appliquant ces relations pour la courbe expérimentale d'élution on obtient les valeurs ci-dessous :

|          |               |                |
|----------|---------------|----------------|
| Tl(III), | $N = 145,0$ , | $H = 5,17$ mm, |
| Al(III), | $N = 148,0$ , | $H = 5,07$ mm, |
| In(III), | $N = 143,4$ , | $H = 5,2$ mm,  |
| Ga(III), | $N = 147,2$ , | $H = 5,1$ mm,  |

qui conduisent aux valeurs moyennes,  $N = 145,9$  et  $H = 5,14$  mm.

La valeur très basse de  $H$  indique une efficacité supérieure de la colonne chromatographique utilisée et concorde avec l'observation selon laquelle la grandeur  $H$  dépend du rayon des granules de l'échangeur.

Les valeurs des coefficients de distribution des ions Al(III), Ga(III), In(III) et Tl(III) lors de la sorption sur la cellulose phosphate  $P_w$ -Serva avec le mélange HCl 0,5 M — éthanole (60%) (Fig. 3) prouve la possibilité d'utiliser ce mélange comme éluant des ions ci-dessus.

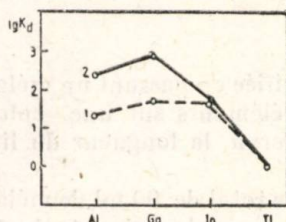


Fig. 3. — Distribution des ions Al(III), Ga(III), In(III), Tl(III) sur cellulose phosphate  $P_w$ -Serva: 1 — solution aqueuse HCl 0,5 M; 2 — mélange 40% HCl 0,5 M — 60% alcool éthylique.

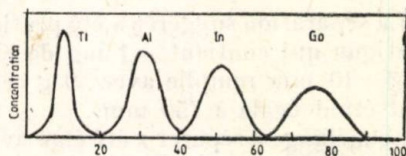
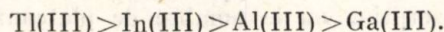


Fig. 4. — Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur cellulose phosphate  $P_w$ -Serva avec l'éluant 40% HCl 0,5 M — 60% alcool éthylique.

La séparation des ions a été réalisée à l'aide d'une colonne semblable à celle utilisée dans le cas précédent. l'ordre d'élution étant la suivante :



La courbe expérimentale d'élution est représentée dans la Fig. 4.

### 3.2. Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur la cellulose phosphate $P_{11}$ -Whatman

La séparation des ions sur la cellulose phosphate  $P_{11}$ -Whatman a été étudiée en utilisant les mélanges eau — solvant organique avec une acidité 1 M en HCl, qui contient 60% acétone, 40% tétrahydrofurane, respectivement 20% dioxane [13].



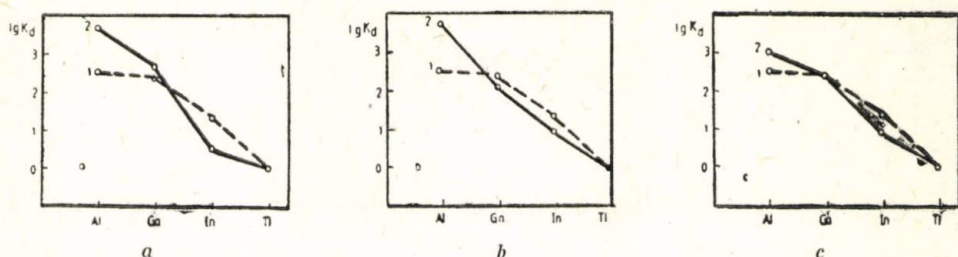


Fig. 5. — Distribution des ions Al(III), Ga(III), In(III), Tl(III) sur cellulose phosphate  $P_{11}$ -Whatman : 1 — solution aqueuse HCl 1 M ; 2 — solution HCl 1 M avec 60 % acétone (a), 40 % tétrahydrofurane (b) et 20 % dioxane (c).

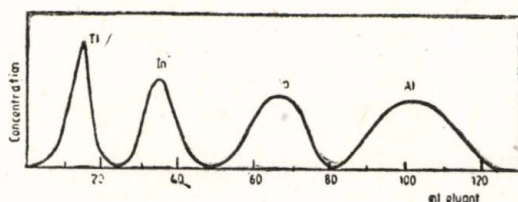


Fig. 6. — Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur colonne avec cellulose  $P_{11}$ -Whatman en utilisant comme éluant le mélange HCl 1 M — 60 % acétone.

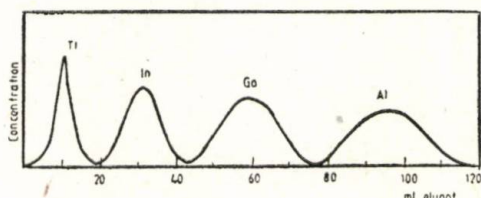


Fig. 7. — Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur cellulose  $P_{11}$ -Whatman avec l'éluant 60 % HCl 1 M — 40 % tétrahydrofurane.

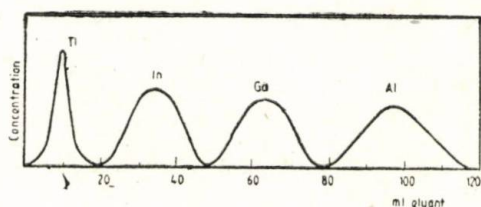


Fig. 8. — Séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur cellulose  $P_{11}$ -Whatman avec l'éluant 80 % HCl 1 M — 20 % dioxane.

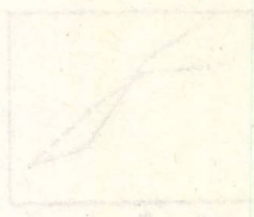
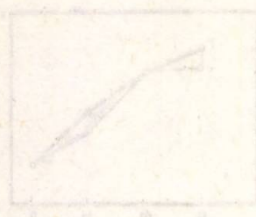


Fig. 2. Dependence of the function  $\Phi(\eta)$  on the parameter  $\eta$  for different values of  $\alpha$ : (a)  $\alpha = 0.1$ ; (b)  $\alpha = 0.2$ ; (c)  $\alpha = 0.3$ . The curves are calculated for  $\beta = 0.1$  and  $\gamma = 0.1$ .

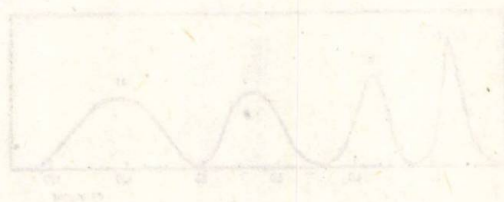


Fig. 3. Dependence of the function  $\Phi(\eta)$  on the parameter  $\eta$  for different values of  $\alpha$ : (a)  $\alpha = 0.1$ ; (b)  $\alpha = 0.2$ ; (c)  $\alpha = 0.3$ . The curves are calculated for  $\beta = 0.1$  and  $\gamma = 0.1$ .

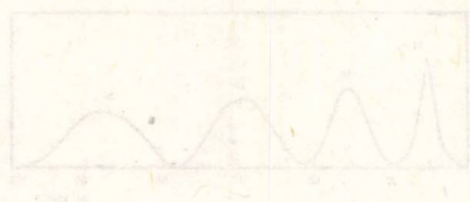


Fig. 4. Dependence of the function  $\Phi(\eta)$  on the parameter  $\eta$  for different values of  $\alpha$ : (a)  $\alpha = 0.1$ ; (b)  $\alpha = 0.2$ ; (c)  $\alpha = 0.3$ . The curves are calculated for  $\beta = 0.1$  and  $\gamma = 0.1$ .



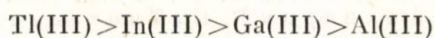
Fig. 5. Dependence of the function  $\Phi(\eta)$  on the parameter  $\eta$  for different values of  $\alpha$ : (a)  $\alpha = 0.1$ ; (b)  $\alpha = 0.2$ ; (c)  $\alpha = 0.3$ . The curves are calculated for  $\beta = 0.1$  and  $\gamma = 0.1$ .



Les valeurs des coefficients de distribution lors de la sorption sur la cellulose  $P_{11}$  de la solution aqueuse 1 M d'acide chlorhydrique et respectivement des mélanges avec des solvants organiques sont présentées dans la Fig. 5.

La représentation graphique exige l'utilisation des systèmes à base de solvants organiques comme éluants pour la séparation quantitative des éléments étudiés.

Les séparations ont été effectuées sur une colonne avec la longueur  $l = 500$  mm et le diamètre  $\varnothing = 10$  mm, qui contient 7,5 g cellulose phosphate  $P_{11}$ -Whatman. Les courbes d'éluion pour les trois (systèmes) mélanges sont symétriques, l'ordre d'éluion étant le même à savoir :



(v. Figs. 6...8).

Pour déterminer l'efficacité de la colonne chromatographique dans le cas de l'utilisation du mélange 40% HCl 1 M — acétone 60%, on a calculé les valeurs  $N$  et  $H$  :

|          |                |                |
|----------|----------------|----------------|
| Tl(III), | $N = 118,4$ ,  | $H = 4,22$ mm, |
| In(III), | $N = 113,12$ , | $H = 4,42$ mm, |
| Ga(III), | $N = 116,8$ ,  | $H = 4,28$ mm, |
| Al(III), | $N = 121,6$ ,  | $H = 4,11$ mm, |

avec les valeurs moyennes  $N = 117,5$  et  $H = 4,26$  mm.

L'accroissement des facteurs de séparation des ions dans des mélanges eau — solvant organique par rapport aux systèmes aqueux est dû à la modification de la distribution des ions à échanger.

Les constituants organiques à basse polarité produisent, d'une part, la diminution, même la destruction de l'enveloppement de hydratation des ions, et d'autre part, l'inhibition préférentielle de la cellulose ionitique.

L'influence différente de la présence des solvants organiques exercée sur la séparation des ions étudiés dépend aussi de l'acidité du milieu.

#### 4. Conclusions

1. L'étude du comportement à la sorption des ions Al(III), Ga(III), In(III) et Tl(III) sur des celluloses phosphate indique la possibilité de les séparer.

2. Les possibilités de séparation des éléments étudiés, sur des celluloses ionitiques, s'élargissent considérablement lorsqu'on utilise des mélanges eau — solvants organiques.

3. On a suggéré et vérifié par voie expérimentale les séparations suivantes : a) séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur la cellulose phosphate  $P_w$ -Serva avec l'éluant 20% HCl 0,01 M — 80% alcool méthylique ou 40% HCl 0,5 M — 60% alcool éthylique ; b) séparation des ions Al(III), Ga(III), In(III) et Tl(III) sur la cellulose phosphate  $P_{11}$ -Whatman

avec HCl 1 M — solvant organique (60% acétone, 40% tétrahydrofurane ou 20% dioxane).

4. On a estimé l'efficacité des colonnes chromatographiques par le calcul des grandeurs  $N$  et  $H$ .

Reçue le 18 septembre 1987

Institut Polytechnique, Jassy,  
Chaire de Chimie Anorganique  
et Analytique

#### BIBLIOGRAPHIE

1. Kraus K. A., Nelson F., Smith G. W., J. Phys. Chem., **58**, 11 (1954).
2. Горокова А. Н., Алимарин И. П., Тинтевич Е. П., ЖНХ, **11**, 191 (1966).
3. Шишкова Л. Г., Докл. Болг. АН, **24**, 10, 1 369; (1971); Ibid., **25**, 10, 1371 (1972).
4. Казанцев Е. И., Плюснин А. В., Изв. ВУЗ, Хим. Технол., **12**, 2, 300 (1974).
5. Тинтевич Е. П., Алимарин И. П., Горокова А. П., Вестник МГУ, серия Химия, **24**, 1, 91 (1969).
6. Korkisch J., Hazan I., Analyt. Chem., **36**, 12, 2308 (1964); Ibid., **27**, 707 (1965).
7. Strelow F.W.E., Van Zyl C.R., Bothma C.J.C., Analyt. Chim. Acta, **45**, 1, 81 (1969).
8. Strelow F.W.E., Victor A. H., Talanta, **19**, 9, 1019 (1972).
9. Strelow F.W.E., Talanta, **27**, 3, 231 (1980).
10. Gagliardi E., Brodar B., Chromatographye, **2**, 6, 267 (1969).
11. Soljic Z., Turina S., Z. analyt. Chem., **257**, 5, 348 (1971).
12. Bilbă D., Fișel S., Mikrochim. Acta, 985 (1974).
13. Фишел С., Былбэ Д., ЖАХ, **30**, 7, 1 317 (1975)

#### SEPARAREA IONILOR DE Al(III), Ga(III), In(III) ȘI Tl(III) PE CELULOZE FOSFAT PRIN CROMATOGRAFIE PE COLOANĂ

(Rezumat)

Factorii de separare ai aluminiului (III), galiului (III), indiului (III), taliului (III) cresc considerabil în amestecuri apă—solvenți organici.

Cu ajutorul unor coloane conținând celuloze fosfat ( $P_w$  și  $P_{11}$ ) și eluanți convenabili (amestecuri apă—solvenți organici) s-au realizat separări cantitative ale celor patru elemente aflate în amestec.



## MOLECULAR SIEVES NaX AS STATIONARY PHASES FOR THIN LAYER CHROMATOGRAPHY

### III. SEPARATION OF SOME ORGANIC DYES

BY

ANIȘOARA BOLD, ANGELA POPA, MARIA GĂBURICI, EVELINE POPOVICI and  
M. CRUCEANU

#### 1. Introduction

Some results regarding the possibility and technique of preparation of a molecular sieves adhesive layer on glass plates for thin layer chromatography (S.L.C.) as well as the experimental data referring to the separation of certain inorganic cations and organic compounds have been reported in a previous paper [1].

Also the separation of some strong acid inorganic cations from mixture, having their diameter much larger than that of the access window in molecular sieve, has been investigated and some assumptions concerning the separation mechanism of them have been formulated. On the basis of some correlations between the  $R_f$  values and thermodynamic quantities of the ion-exchange in a solvent system as mobil phase it was found that in the case of the investigated cations, their migration and separation takes places by ion-exchange process [2].

The present paper deals with some theoretical and experimental aspects in connection with the separation on NaX zeolite of some weak ionic components with large geometrical size such as some acid or basic organic dyes.

#### 2. Experimental

The molecular sieve, employed as stationary phase, was of the NaX type, supplied by Natrium Products Works, Govora, and preparation of plates as well as their developing was made as previously described [1].

The experiments were performed with 0.5% aqueous solutions of the following acid dyes: Red acid, Yellow R acid, Blue 5 R acid and basic dyes: Red melacryl BL, Yellow melacryl and Blue melacryl BLK.

The developing solvents were selected from Macek and Prochazka's elutropic series [3] and, localization and identification of the chromatographic spots was carried out visually.

#### 3. Results and Discussion

In order to evaluate the separation ability of the selected solvents, first was made some tests according to microcircular technique developed by Stahl [4] and Randerath [5]. The results of the tests are sum-



marized in Table 1. As it can be seen in Table 1, in the selected solvents the two types of dyes do not exhibit large dissimilarities and in both cases the solvents with little polarity hinder the migration, while those with high polarity favour excessively it carrying the dye with their front. Consequently, the developings were carried out with binary or ternary mixtures of solvents, chosen in such a manner that the compensation of the two behaviours to be realized, using orientatively the calculated value of dielectric constant.

Table 1

*Migration Behaviour of the Investigated Dyes in certain Solvents*

| Run | Solvent             | Dielectric constant | Acid dyes |   |   | Basic dyes |   |   |
|-----|---------------------|---------------------|-----------|---|---|------------|---|---|
|     |                     |                     | R*)       | G | A | R**)       | G | A |
| 1   | Nitrobenzene        | 36.4                | +         | + | + | +          | + | + |
| 2   | Methanol            | 31.2                | ∞         | ∞ | ∞ | ∞          | ∞ | ∞ |
| 3   | Isopropanol         | 26.0                | +         | ∞ | ∞ | ∞          | + | ∞ |
| 4   | Ethanol             | 25.8                | ∞         | ∞ | ∞ | ∞          | ∞ | ∞ |
| 5   | Acetone             | 21.5                | ∞         | ∞ | ∞ | ∞          | ∞ | ∞ |
| 6   | Methyl ethyl ketone | 18.0                | +         | + | + | +          | + | + |
| 7   | Amyl alcohol        | 16.0                | +         | + | + | ∞          | ∞ | ∞ |
| 8   | Benzyl alcohol      | 13.0                | +         | ∞ | ∞ | ∞          | ∞ | ∞ |
| 9   | Chloroform          | 5.1                 | 0         | 0 | 0 | ∞          | 0 | ∞ |
| 10  | Toluene             | 2.3                 | 0         | 0 | 0 | +          | 0 | + |
| 11  | Benzene             | 2.24                | 0         | 0 | 0 | 0          | 0 | 0 |
| 12  | Heptane             | 1.97                | 0         | 0 | 0 | 0          | 0 | 0 |

\*) R — Red acid ; G — Yellow acid ; A — Blue 5R acid.

\*\*) R — Melacryl Red BL ; G — Melacryl yellow ; A — Melacryl blue BLK.

∞ — the spots migrate with the developant front ;

+

 — the spots migrate with different rates ;

0 — the spots do not migrate.

A part of the solvents systems and  $R_f$  values obtained experimentally are summarized in Tables 2 and 3.

On the basis of the data from Table 2, in some measure the qualitative observation referring to correlation with dielectric constant of the system is verified and at the same time we get informations that evidence the fact that the separation of dyes mixtures is possible only with solvents systems which have large dielectric constant. The systems which the dielectric constant less than 10, although according with the data in Tables 2 and 3, they allow a certain separation, however they cannot be employed practically because the differences between the  $R_f$  values for acid dyes are very low and, for basic dyes the resolution is not satisfactory enough.

In the systems with high dielectric constant the mixtures of acid dyes should be separated much better, for dielectric constants ranging from 13 to 26 and, the mixtures of the basic dyes in the systems with dielectric constant of 19...21.

Also, the result evidences the fact that from all investigated dyes only Yellow acid R is pure, all the other giving several chromatographic spots are impure.



Table 2

*Solvents Systems and the  $R_f$  Values for Acid Dyes*

| Run      | System of solvents                  | Ratio of solvents V/V | Dielectric constant $\epsilon$ | $R_f$        |               |              |
|----------|-------------------------------------|-----------------------|--------------------------------|--------------|---------------|--------------|
|          |                                     |                       |                                | Red acid     | Yellow acid R | Blue acid 5R |
| $S_1$    | Nitrobenzene—Ethanol                | 3 : 1                 | 33.7                           | 0.95         | 0.92          | 0.95         |
| $S_2$    | Ethanol—Isopropanol                 | 1 : 1                 | 25.9                           | 0.81<br>0.70 | 0.58          | 0.37<br>0.07 |
| $S_3$    | Nitrobenzene—Benzene—Heptane        | 4 : 2 : 1             | 21.7                           | 0.28         | 0.11          | 0.46<br>0.41 |
| $S_4$    | Benzyl alcohol—Nitrobenzene         | 2 : 1                 | 20.3                           | 0.86<br>0.79 | 0.75          | 0.62<br>0.36 |
| $S_5$    | Methyl ethyl ketone—Acetone         | 1 : 1                 | 19.7                           | 0.73<br>0.68 | 0.68          | 0.64<br>0.47 |
| $S_6$    | Nitrobenzene—Toluene                | 1 : 1                 | 19.4                           | 0.20         | 0.10          | 0.36<br>0.30 |
| $S_7$    | Benzyl alcohol—Ethanol—Chloroform   | 2 : 1 : 1             | 14.2                           | 0.71<br>0.60 | 0.65          |              |
| $S_8$    | Benzyl alcohol—Amyl alcohol         | 2 : 1                 | 13.9                           | 0.74<br>0.70 | 0.66          | 0.52<br>0.46 |
| $S_9$    | Toluene—Methyl ethyl ketone—Acetone | 1 : 1 : 1             | 13.8                           | 0.41<br>0.30 | 0.21          | 0.46<br>0.18 |
| $S_{10}$ | Benzene—Methyl ethyl ketone—Acetone | 4 : 2 : 1             | 9.5                            | 0.11         | 0.08          | 0.12         |

Table 3

*Solvents Systems and the  $R_f$  Values for Basic Dyes*

| Run   | System of solvents                  | Ratio of solvents V/V | Dielectric constant $\epsilon$ | $R_f$                |                      |                   |
|-------|-------------------------------------|-----------------------|--------------------------------|----------------------|----------------------|-------------------|
|       |                                     |                       |                                | Melacryl red BL      | Melacryl yellow      | Melacryl blue BLK |
| $S_1$ | Ethanol—Isopropanol                 | 1 : 1                 | 25.9                           | 0.95<br>0.95<br>0.98 | 0.75                 | 0.73              |
| $S_2$ | Nitrobenzene—Benzene—Heptane        | 4 : 2 : 1             | 21.7                           | 0.64<br>0.45         | 0.42<br>0.31<br>0.16 | 0.80<br>0.52      |
| $S_3$ | Nitrobenzene—Toluene                | 1 : 1                 | 19.4                           | 0.62<br>0.52<br>0.41 | 0.39<br>0.33<br>0.15 | 0.79<br>0.56      |
| $S_4$ | Toluene—Methyl ethyl ketone—Acetone | 1 : 1 : 1             | 13.8                           | 0.82<br>0.55         | 0                    | 0.47              |
| $S_5$ | Benzene—Methyl ethyl ketone—Acetone | 4 : 2 : 1             | 9.5                            | 0<br>0.87            | 0                    | 0.79              |

The shape of the chromatographic spots (Fig. 1) and resolution obtained make possible utilization for analysis and separation of the mixture of acid dyes the systems with alcohols ( $S_2$ ,  $S_8$  — Table 2) and for basic dyes the systems of solvents with nitrobenzene and hydrocarbons ( $S_3$  and  $S_5$  — Table 3).

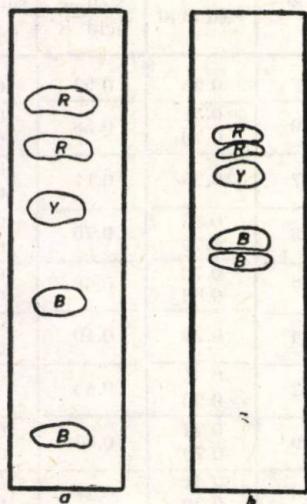


Fig. 1. — Separation of some mixtures of acid dyes on zeolite NaX: a — mobile phase: ethanol — isopropanol (1 : 1 V/V); b — mobile phase: benzyl alcohol — amyl alcohol (2 : 1 V/V).

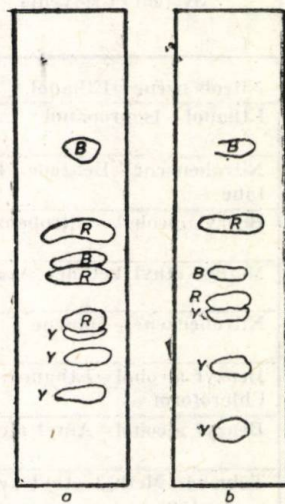
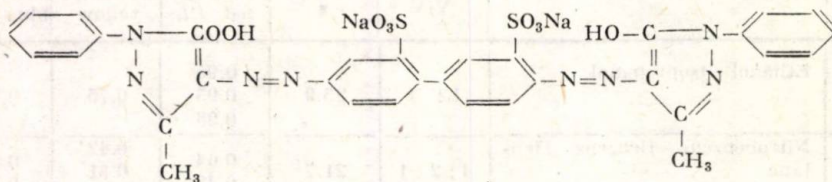


Fig. 2. — Separation of some mixtures of basic dyes on zeolite NaX: a — mobile phase: nitrobenzene — toluene (1 : 1 V/V); b — mobile phase: nitrobenzene — benzene — heptane (4 : 2 : 1, V/V).

Because in each class of dyes the migration rate and  $R_f$  value are dependent on the polarity of solvent system, it is clear that in this case the separation by S.L.C. on the molecular sieves NaX takes place according with an adsorption mechanism by interactions of multipolar type. Although, the investigated dyes, by their structure, has not a permanent dipole, e.g. Yellow acid R:



Yellow acid R

However, according to Gorel [6], the molecules provided with polar groups can be adsorbed on the polar surface of stationary phase and, according to Chessik *et al.* [7] statement, the value of adsorption energies of different polar groups in molecule is proportional to their dipolar moment. These general remarks, valid for stationary phases of different nature, in the case



of molecular sieves become more particular, first, due to the strong polar character of the zeolite surface, caused by the OH groups bonded at silicon atoms in their structure and on the other hand due to the particular porosity structure of these adsorbants.

For example while in silicagel the porous structure has a large pores size distribution from any tens to any hundred of Angstroms, the value of mean diameter being almost 30...100 Å, at the molecular sieves this distribution includes only one pore size. In this case, the curve of Gaussian's distribution becomes a single line, which in the case, e.g. for the molecular sieve NaX, is situated at the value of 13 Å. Due to this fact, at inner adsorption surfaces are accessible only the molecules of geometrical size less than „zeolite windows“. However, for investigated dyes the values regarding the molecule dimensions are not available due to their state in solution of different polarities, these data should have only an orientative value, but taking into account some known values, e.g. critical diameter of benzene (5.60 Å), as well as mobility of the molecular components around the chain axis, let us consider that on zeolite NaX with 13 Å windows, separation of the investigated dyes took place by an adsorption process of them in both inner and outer crystalline structure.

To verify these hypotheses, the separation attempts were carried out, under the same conditions, but with stationary phases made up of the molecular sieve NaA. These molecular sieves, having the window of 4 Å is sure that any access possibility of dye molecules inside the zeolite is excluded.

Table 4

*Comparative Separations of Red Acid R and Blue Acid 5R on the Molecular Sieves NaX and NaA*

| System of solvents                  | Ratio of solvents V/V | Dielectric constant $\epsilon$ | $R_f/\text{NaX}$ |             | $R_f/\text{NaA}$ |             |
|-------------------------------------|-----------------------|--------------------------------|------------------|-------------|------------------|-------------|
|                                     |                       |                                | Red acid R       | Blue acid R | Red acid R       | Blue acid R |
| Ethanol— <i>isopropanol</i>         | 1:1                   | 25.9                           | 0.81             | 0.37        | $\infty$         | $\infty$    |
| Methyl ethyl ketone—acetone         | 1:1                   | 19.7                           | 0.73             | 0.64        | $\infty$         | $\infty$    |
| Benzyl alcohol— <i>amyl alcohol</i> | 2:1                   | 13.8                           | 0.74             | 0.52        | $\infty$         | $\infty$    |

The data of Table 4 show that independently from the dielectric constant of the employed solvents system, the tested dyes migrate with the solvent, fact that shows that in the case of zeolite NaA no adsorption phenomenon takes places, while on zeolite NaX the separation is due to this phenomenon.

At the same time, however the surface is equal polar, but separation takes place only on zeolite NaX, then we can make the remark that in the case of weak ionic components, their separation is carried out only by adsorption.



#### 4. Conclusions

Investigation of the possibility of some acid and basic dyes to be analysed by S.L.C. on zeolite NaX has shown that separation can be realized with high resolution and that the  $R_f$  values depend on both dielectrical constant of mobil phase and the nature of the employed solvents. The separation of some weak ionic character organic components on zeolite NaX takes place according with a separation mechanism of adsorption, proving our initial hypothesis.

The developed method can be employed successfully for the purity determination of some dyes as well as for analysis of their mixtures.

Received, July 7, 1987

Polytechnic Institute, Jassy,  
Department of Inorganic  
and Analytical Chemistry  
and  
Department of General  
Chemistry and Technology

#### REFERENCES

1. Bold A., Popa A., Cruceanu M., Popovici E., Rev. Chimie, **35**, 12, 1123 (1984).
2. Bold A., Popa A., Cruceanu M., Găburici M., Popovici E., Rev. Roum. Chim. (sous presse),
3. Hais I. M., Macek K., *Cromatografia pe hirtie*, (transl. from Czech.). Ed. Tehn., București, 1960, 112.
4. Stahl E., *Dünnschicht-Chromatographie, ein Laboratoriumshandbuch*, II. Ed., Springer Verlag, Berlin, 1967, 125.
5. Randerath K., *Thin-Layer Chromatography*. Ed. II, Academic Press, New York, 1966, 53, 67.
6. Corel J. P., Bull. Soc. Chim. France, 653 (1964).
7. Chessik J. J., Canad. J. Chem., **33**, 251 (1965).

#### SITE MOLECULARE NaX FAZE STAȚIONARE ÎN CROMATOGRAFIA PE STRAT SUBȚIRE

##### III. Separarea unor coloranți organici

##### (Rezumat)

S-a studiat posibilitatea de separare a unor coloranți acizi și bazici prin cromatografia pe strat subțire cu sită moleculară NaX.

S-au folosit mai multe sisteme de dezvoltare.

S-au calculat valorile  $R_f$  și s-a stabilit că acestea depind atât de valoarea constantei dielectrice a sistemului de dezvoltare cât și de natura solvenților componenți ai acestuia.

Referitor la mecanismul de separare s-a formulat ipoteza că acesta se desfășoară numai pe baza unui fenomen de adsorbție moleculară.



## Sr(II) AND Ba(II) SORPTION AND SEPARATION ON 4(4'-AZOBENZYLCELLULOSE)1-HYDROXY-2-CARBOXYBENZENE

BY

TINCA ONOFREI

### 1. Introduction

In several previous papers [1]...[3] we have published data referring to Be(II), Mg(II), Ca(II), Zn(II), Cd(II) and Hg(II) sorption and separation on 4(4'-azobenzylcellulose)1-hydroxy-2-carboxybenzene used as a chelating sorbent.

We carried these researches further, investigating Sr(II) and Ba(II) sorption on the same sorbent as well as the possibility of separating chromatographically these two elements.

### 2. Experimental

4(4'-azobenzylcellulose)1-hydroxy-2-carboxybenzene was obtained by diazotation of PAB-cellulose and coupling it with salicylic acid in a slightly alkaline medium.

In order to assess the mechanism of Sr(II) and Ba(II) sorption on 4(4'-azobenzylcellulose)1-hydroxy-2-carboxybenzene the following determinations have been made:

- a) Dependence of distribution coefficients ( $K_d$ ) vs. pH, at 25°C.
- b) Sorption isotherms at 25°C.
- c) Sorption isobars between 0° and 100°C.
- d) Determination of apparent free enthalpy.
- e) Reflectance electronic spectra.
- f) IR spectra of the sorbent before and after sorption, between 400 and 4 000  $\text{cm}^{-1}$ .

The distribution coefficients were determined by an equilibrium method that was reached by stirring 0.5 g sorbent with 20  $\text{cm}^3$  standard solution of  $\text{Sr}(\text{ClO}_4)_2$  (70.4  $\mu\text{g}$  Sr (II)/ $\text{cm}^3$ ) and  $\text{Ba}(\text{ClO}_4)_2$  (81.9  $\mu\text{g}$  Ba(II)/ $\text{cm}^3$ ) with a specified pH, at a constant temperature, for an hour. The solid phase was separated by filtering. The equilibrium pH ( $\text{pH}_e$ ) was measured in the aqueous phase. Sr(II) and Ba(II) excess was spectrophotometrically determined by

the *o*-cresolphthaleincomplexone method [4]. For isotherms, standard solutions with concentrations ranging from  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-2}$  M were used.

### 3. Results and Discussions

From the study of the dependence of the distribution coefficients vs. pH, there follows that Sr(II) sorption increases gradually from  $\text{pH}_e = 2.2$  ( $K_d = 2.00$ ) to  $\text{pH}_e = 4.3$  ( $K_d = 4.78$ ), while Ba(II) sorption increases from  $\text{pH}_e = 2.8$  ( $K_d = 2.17$ ) to  $\text{pH}_e = 4.7$  ( $K_d = 41.70$ ). For all the determinations the equilibrium pH was experimentally found to be lower than the pH of the solution that comes in touch with the sorbent.

The sorption isotherms for Sr(II) and Ba(II) (Fig. 1) assume different shapes. The sorption isotherm for Sr(II) shows an overlapping of the chemical sorption over the physical sorption, the latter being prevalent. The sorption isotherm for Ba(II) assumes a shape that pleads in favour of a combined process of physical and chemical sorption, chemisorption being prevalent.

The study of the sorption isobars for Sr(II) and Ba(II) (Fig. 2) lead to the same conclusions as in the previous case. The decrease of the distrib-

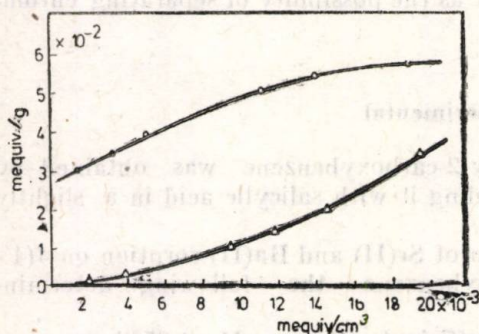


Fig. 1. — The sorption isotherms at  $\text{pH}_e = 4.3$  and  $25^\circ\text{C}$ :  $\Delta$  — Sr(II);  $\circ$  — Ba(II).

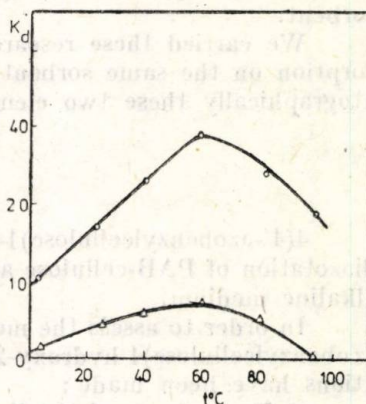


Fig. 2. — The sorption isobars between  $0^\circ\text{C}$ ... $100^\circ\text{C}$ :  $\Delta$  — Sr(II);  $\circ$  — Ba(II).

ution coefficients above  $62^\circ\text{C}$  is attributed to the partial degradation of the sorbent.

The apparent free enthalpy, calculated with the help of the relation

$$\Delta G = -RT \ln K,$$

has the value  $-670$  cal/mol for Ba(II), which shows an overlapping of the chemical sorption over the physical one. For Sr(II) this value cannot be calculated since the obtained data for its isotherm do not meet the conditions required by Nikolski's relation [5], [6].



The sorbent is yellow and displays an absorption maximum at 440 nm (Fig. 3, curve 1), which shifts to 455 nm after complexing (Fig. 3, curve 2).

From the study of IR spectra there follows that modifications arise only with the  $\text{—COOH}$  groups of the salicylic acid, the complexes behaving as carboxylates in which the vibration frequencies assume intermediary values between  $\nu_{\text{C=O}}$  and  $\nu_{\text{C—O}}$ . The  $\text{—OH}$  group is screened by the hydroxylic groups of cellulose. The frequencies of valency vibration of the azo group are not modified after the sorption process occurs, which lead to the conclusion that the formation of chelates occurs with the carboxyl and hydroxyl groups:

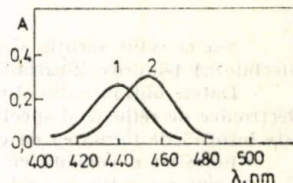
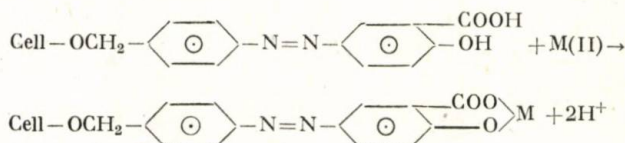


Fig. 3. — The reflectance electronic spectrum: before (curve 1) and after sorption (curve 2).



The decrease of pH during the sorption process as well as the data yielded by IR spectra and the electronic reflectance spectra lead to the conclusion that the physical sorption of Sr(II) and Ba(II) is accompanied by an ionic exchange and by a reaction with formation of chelates whose scheme was given above.

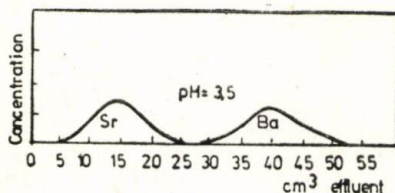


Fig. 4. — Separation of Sr(II) from Ba(II).

The satisfactory separation of the two elements was carried out on a column (250 mm long and 10 mm in diameter), filled with 4 g sorbent, using as eluent a solution of 0.1 M perchloric acid - sodium perchlorate with  $\text{pH} = 3.5$  (Fig. 4). The obtained results represented in the figure

hold true in the domain of a ratio of  $1/10$  between the components.

*Received, May 8, 1987*

*Polytechnic Institute, Jassy,  
Department of Inorganic and  
Analytical Chemistry*

## REFERENCES

1. Ungurenaşu-Onofrei T., Fişel S., Proc. 3<sup>rd</sup> Nat. Anal. Chem. Conf., Braşov Romania, **4**, 61 (1971).
2. Ungurenaşu-Onofrei T., Fişel S., Rev. Chim., **24**, 926 (1973).
3. Ungurenaşu-Onofrei T., Fişel S., Chem. Analyt. (Warszawa), **19**, 257 (1974).
4. Pollard F.H., Martin J. V., Analyst, **81**, 348 (1956).
5. Никольский Б. П. К.т.н. дисс., Ленинград, 1939.
6. Никольский Б. П., ЖПХ, **8**, 1935 (1939).

# SORBȚIA ȘI SEPARAREA Sr(II) ȘI Ba(II) PE 4(4'-AZOBENZILCELULOZA) 1-HIDROXI-2-CARBOXIBENZEN

(Rezumat)

S-a cercetat sorbția și separarea Sr(II) și Ba(II) pe polimerul chelatizant 4(4'-azobenzilceluloza) 1-hidroxi-2-carboxibenzen.

Datele obținute din studiul dependenței sorbției față de pH, izoterme, izobare, spectre electronice de reflexie și spectre IR au condus la concluzia că sorbția fizică a Sr(II) și Ba(II) este însoțită de formarea de chelați.

Folosind o coloană cu umplutură de 4(4'-azobenzilceluloza) 1-hidroxi-2-carboxibenzen și ca eluent o soluție de acid percloric—perclorat de sodiu 0,1 M cu pH = 3,5, cele două elemente au fost separate în mod satisfăcător.





# CATALYTIC REMOVAL OF OXYGEN FROM THE NITROGEN — HYDROGEN—OXYGEN MIXTURE USED IN THE AMMONIA SYNTHESIS

BY

ANA TARHON and GH. IONESCU

## 1. Introduction

The main industrial procedures for obtaining nitrogen and hydrogen lead to their impurification with other gases, among which oxygen. These impurities are, in the reaction of ammonia synthesis, the so called „inert gases“.

The influence of the inert gas on the degree of conversion of a chemical reaction is analysed by means of the thermodynamic equation of the form [1] :

$$(1) \quad \left( \frac{\partial \xi}{\partial n_{0j}} \right)_{p, T, n_{0i} \neq j} = \frac{x_j \sum v_i - v_j}{n_j [\sum v_i^2 / n_i - (\sum v_i)^2 / \sum n_i]},$$

where :  $\xi$  — the degree of conversion (advancement) of the reaction ;  $n_{0j}$  — initial number of moles of the inert gas  $j$  ;  $v_j$ ,  $x_j$ ,  $n_j$  — the stoichiometric coefficient of the inert gas, the mole fraction and the number of moles of the mixture with nitrogen and hydrogen, respectively ;  $\sum n_i$ ,  $\sum v_i$  and  $\sum v_i^2 / n_i$  are quantities referring to the reaction of ammonia synthesis.

From the thermodynamic point of view an inert gas with respect to a certain reaction is defined by the condition :

$$(2) \quad v_j = 0.$$

Mathematically it can be demonstrated that the expression in the square brackets, (Eq. (1)), is a positive one. Since  $x_j$  and  $n_j$  are, by their meaning, positive quantities, the sign of the derivative of this equation will be given only by the sign of the  $\sum v_i$  quantity.

By considering, for the ammonia synthesis, the stoichiometric equation :



the quantity  $\sum v_i$  has the value equal to  $-2$ , hence is negative. It follows that the derivative  $(\partial \xi / \partial n_{0j})$ , in conditions of preassure, temperature and constant number of moles of the other gases (excepting for the inert gas  $j$ ), will be negative. Hence, the increase of oxygen concentration in the nitrogen—hydrogen mixture will result in decreasing the ammonia yield. Starting from a certain concentration of oxygen (inert gas) in the nitrogen—hydrogen mixture the lowering of the ammonia yield becomes significant and the oxygen removal from the reacting gases becomes necessary.

In the modern industrial procedures the oxygen removal from the nitrogen—hydrogen mixture can be accomplished by passing the nitrogen—hydrogen—oxygen mixture over a suitable catalyst, for the combustion reaction,



to take place at the ambient temperature and the heat evolved in this highly exothermic reaction ( $-571.9$  KJ/mol  $O_2$ ) [2] to be taken off by introducing in the catalytic reactor some heat



recovery devices (economizers) and used in various technological purposes, which contributes to the energetic optimization of the whole industrial process of ammonia synthesis.

The present paper is aimed to test the catalyst H-14-19 with 0.25% Pd, supplied by the firm „Katalysatoren-Werke Houdry-Hüls GMBH-D 4 370, Marl“, in the reaction of oxygen removal from the nitrogen—hydrogen—oxygen mixture, by combustion reaction (4). The catalyst characteristics are found in the firm catalogue [3].

## 2. Experimental, Results and Discussion

For investigating the above discussed problems a technological process was sketched and an appropriate equipment, at a laboratory scale, has been accomplished (Fig. 1).

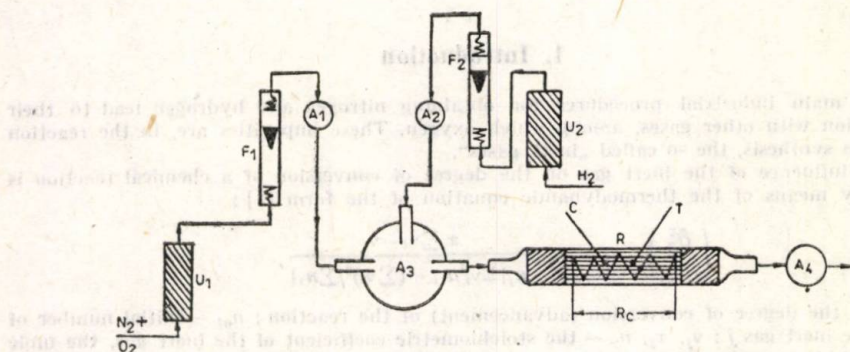


Fig. 1. — Technological flux and principle diagram of installation for catalytic elimination of oxygen from mixture nitrogen—hydrogen—oxygen:  $R$  — reactor;  $C$  — catalyst;  $R$  — heat recuperator;  $T$  — thermometer;  $U_1$ ,  $U_2$  — dryer vessel with silicagel;  $F_1$ ,  $F_2$  — flowmeters;  $A_3$  — reagent gas-mixer;  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$  — analysis points.

The reaction development has been followed by the gas-chromatography on a „molecular-sieve“ column using argon as gas carrier. The molecular sieves exhibit the advantages of retaining quickly and totally the water vapours from the initial reagent mixture and from the reaction products. The chromatograph used was of Pye 104 type, with Orion KTS recorder; the catharometer temperature  $50^\circ\text{C}$ ; the oxygen flow-rate, measured by the put out of level of sulphuric acid ( $\rho=1.4$ ) with a differential manometer, has  $\Delta h = 25$  mm col.  $H_2SO_4$ ; the bridge current was 50 mV; different gas volumes injected and various sensitivities.

To illustrate the accuracy of analysis as regards the possibility of component separation ( $N_2$ ,  $O_2$ ,  $H_2$ ) in Fig. 2 a chromatogram of the initial mixture of these gases (mixer  $A_3$ ) and one of the reaction product at the outlet of the catalytic reactor ( $A_4$  node) are showed. It can be noticed that in our conditions the retention times sensibly differ, so that distinct, well individualized peaks for each gas in mixture are obtained.



The experimental data indicated a particularly high activity of the catalyst used with respect to the reaction (4). Thus, if a  $H_2/O_2$  volume ratio equal at least with the stoichiometric ratio (2/1) is used, the oxygen will be absent in the reaction products even at the ambient temperature.

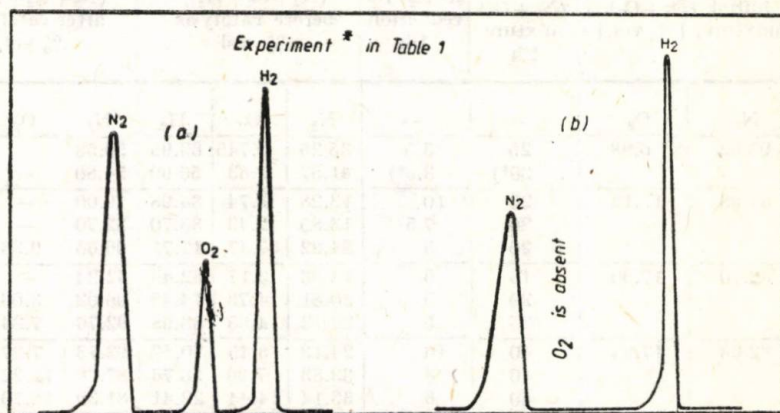


Fig. 2. — Chromatogram regarding the accuracy of the used analysis: *a* — chromatogram before the catalysis:  $V = 1$  mL,  $S = 50$  for  $N_2$  and  $O_2$  and  $S = 500$  for  $H_2$ ,  $v$  (paper) = 76.2 cm/h,  $h = 25$  mm column  $H_2SO_4$ ,  $t = 50^\circ C$ , argon—mobile phase, molecular sieves—stationary phase; *b* — chromatogram after catalysis,  $S = 500$  for both gases; other conditions are given to point *a*.

In case of the reactor used (diameter  $\varnothing = 20$  mm), containing 125 g catalyst, 750 mm lengthwise, the temperature was maintained at  $20^\circ C$  by means of a cooling coil over the whole length of the catalyst layer. As cooling liquid water has been used, the water flow rate being correlated with the flow rate of the reaction mixture (nitrogen—hydrogen—oxygen) and with the  $H_2/O_2$  ratio.

The efficient cooling of the reactor is required, on one hand, for the energetic optimization of the overall process of ammonia synthesis and on the other hand for avoiding the attaining of ignition temperature (explosion in closed space) of the hydrogen—oxygen mixture due to of combustion reaction ( $580^\circ \dots 590^\circ C$ ) [4].

To modify the initial composition of the nitrogen—hydrogen—oxygen mixture, in the mixer ( $A_3$ ) a mixture of nitrogen and oxygen of constant composition and a hydrogen flux are separately introduced. By varying the ratio of flow rates of the two gas fluxes which penetrate in the mixing chamber, nitrogen—hydrogen—oxygen mixtures of various concentrations have been obtained. The analysis of the composition of these mixtures prior to and after passing through the reactor with catalyst (in the nodes  $A_3$  and  $A_4$  respectively), evidenced the change of concentrations of hydrogen and oxygen, as a result of the equation (4), which becomes a reaction of cold combustion [5].

In Table 1 the experimental data for nine run groups are listed. Each group is characterized by a constant concentration of the nitrogen, oxygen mixture, and variable composition of the nitrogen—hydrogen—oxygen mixture in the mixing chamber ( $A_3$ ).



Table 1

## Experimental Data

| Nr. | Composition of initial ( $N_2 + O_2$ ) mixture, [% vol.] |       | Flow rate of ( $N_2 + O_2$ ) mixture l/h | Flow rate of $H_2$ for reduction l/h | Composition of ( $N_2 + O_2 + H_2$ ) before catalysis % vol |       |       | Composition of ( $N_2 + O_2 + H_2$ ) after catalysis % vol. |       |       |
|-----|----------------------------------------------------------|-------|------------------------------------------|--------------------------------------|-------------------------------------------------------------|-------|-------|-------------------------------------------------------------|-------|-------|
|     | $N_2$                                                    | $O_2$ |                                          |                                      | $N_2$                                                       | $O_2$ | $H_2$ | $N_2$                                                       | $O_2$ | $H_2$ |
| 1   | 93.02                                                    | 6.98  | 25                                       | 3.5                                  | 35.25                                                       | 0.745 | 63.99 | 50.58                                                       | —     | 49.42 |
|     |                                                          |       |                                          |                                      | 41.57                                                       | 1.53  | 56.90 | 54.80                                                       | —     | 45.20 |
| 2   | 84.88                                                    | 15.12 | 20                                       | 10                                   | 13.28                                                       | 1.74  | 84.98 | 19.00                                                       | —     | 81.00 |
|     |                                                          |       | 20                                       | 7.5                                  | 13.85                                                       | 2.43  | 83.70 | 32.70                                                       | —     | 67.30 |
|     |                                                          |       | 20                                       | 5                                    | 24.82                                                       | 57.47 | 17.71 | 90.66                                                       | 9.33  | —     |
| 3   | 82.70                                                    | 17.30 | 15                                       | 5                                    | 14.38                                                       | 3.17  | 82.45 | 62.24                                                       | —     | 37.76 |
|     |                                                          |       | 20                                       | 5                                    | 20.81                                                       | 4.73  | 74.45 | 96.92                                                       | 3.08  | —     |
|     |                                                          |       | 25                                       | 5                                    | 26.12                                                       | 4.85  | 68.98 | 92.76                                                       | 7.24  | —     |
| 4   | 82.06                                                    | 17.94 | 40                                       | 10                                   | 24.13                                                       | 5.45  | 70.42 | 92.73                                                       | 7.27  | —     |
|     |                                                          |       | 40                                       | 8                                    | 33.83                                                       | 7.96  | 58.76 | 87.78                                                       | 12.22 | —     |
|     |                                                          |       | 40                                       | 6                                    | 63.14                                                       | 14.44 | 22.41 | 81.30                                                       | 18.70 | —     |
| 5   | 79.10                                                    | 20.90 | 20                                       | 5.5                                  | 17.40                                                       | 2.91  | 79.69 | 95.70                                                       | —     | 4.30  |
|     |                                                          |       | 20                                       | 4                                    | 25.55                                                       | 4.95  | 69.50 | 90.53                                                       | —     | 9.47  |
|     |                                                          |       | 30                                       | 10                                   | 14.13                                                       | 12.50 | 73.37 | 30.10                                                       | —     | 69.90 |
| 6   | 77.68                                                    | 22.32 | 30                                       | 4                                    | 32.39                                                       | 4.45  | 63.16 | 90.50                                                       | —     | 9.50  |
| 7   | 69.00                                                    | 31.00 | 40                                       | 10                                   | 36.58                                                       | 12.27 | 51.15 | 77.15                                                       | 22.40 | 0.45  |
|     |                                                          |       | 40                                       | 5                                    | 46.18                                                       | 15.86 | 37.95 | 77.76                                                       | 22.23 | —     |
| 8   | 63.52                                                    | 36.48 | 30                                       | 12.5                                 | 8.41                                                        | 2.61  | 88.98 | 45.29                                                       | —     | 54.71 |
|     |                                                          |       | 30                                       | 10                                   | 44.27                                                       | 19.10 | 36.63 | 94.10                                                       | 5.90  | —     |
| 9   | 61.70                                                    | 38.30 | 20                                       | 7.5                                  | 7.77                                                        | 2.50  | 89.73 | 88.75                                                       | —     | 11.25 |
|     |                                                          |       | 20                                       | 3.5                                  | 16.70                                                       | 8.69  | 74.60 | 69.50                                                       | 30.50 | —     |

## 3. Conclusions

1. The main conclusion that can be drawn is that at the ambient temperature the activity of the catalyst used is particularly high so that the reaction (4) becomes a „cold combustion reaction“.

2. The reaction (4) is highly exothermic and its development at the specified temperature requires the use of an efficient cooling system in the reactor. Such a system can function as an economizer, thus contributing to the increase of efficiency of the whole synthesis process of ammonia.

3. By using a minimum  $H_2$  to  $O_2$  volume ratio of 2/1 the total consumption of the oxygen from the nitrogen—hydrogen—oxygen mixture is assured, since the rate of equation (4) is very high.

4. The high reaction rate favours short contact times between reagents and catalyst which positively influence the increase of gas rates in passing through the catalyst layer and thus the reactor productivity and size; a smaller reactor will require simpler cooling devices.

Received, January 23, 1987

Polytechnic Institute, Jassy,  
Department of Physical Chemistry



## REFERENCES

1. **Șchiopu M.**, unpublished data.
2. Landolt-Börnstein, *Eigenschaften der Materie in ihren Aggregatzuständen. II. Bd.*, 4. Teil, *Kalorische Zustandsgrößen*. Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961, 181.
3. \* \* \* Katalog *Katalysatoren Houdry-Hüls, Marl*, 1975.
4. \* \* \* *Manualul Inginerului Chimist*. Ed. Tehn., Buc., 1952, 1991.
5. Pancenkov G. M., Lebedev V. P., *Chemical Kinetics and Catalysis*. Mir Publishers, Moscow, 1976, 169.

ELIMINAREA CATALITICĂ A OXIGENULUI DIN AMESTECUL AZOT-HIDROGEN  
UTILIZAT ÎN SINTEZA AMONIAICULUI

(Rezumat)

S-a testat activitatea catalizatorului solid H-14-19 cu 0,25% Pd, în reacția de ardere  $H_2/O_2$ , în scopul purificării de oxigen a amestecului azot-hidrogen, utilizat în sinteza amoniacului. Catalizatorul testat, livrat de Firma „Katalysatoren-Werke Houdry-Hüls GMBH-D 4 370, Marl“, s-a dovedit a fi deosebit de activ, încît reacția are loc cu viteză mare chiar la temperatura mediului ambiant. Pentru menținerea unei astfel de temperaturi este necesară răcirea intensă a reactorului, deoarece reacția fiind puternic exotermă ar putea conduce, în sistem închis, la realizarea temperaturii de aprindere și la explozia sistemului. Recuperarea căldurii de reacție poate contribui la optimizarea energetică a procesului global de sinteză a amoniacului iar eliminarea oxigenului (care constituie un gaz inert în raport cu această reacție de sinteză) conduce la realizarea unui randament practic, în amoniac, cît mai apropiat de randamentul termodinamic posibil.

CONFIDENTIAL

1. The purpose of this document is to provide information regarding the activities of the [redacted] in the [redacted] area. This information is being provided for your information and is not to be distributed outside of your office.

2. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

3. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

4. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

5. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

# CONFIDENTIAL

6. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

7. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

8. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

9. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.

10. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area. The [redacted] has been identified as a [redacted] and is currently active in the [redacted] area.



## GRAVIMETRIC DETERMINATION OF TRIETHYLENETETRAMINE

BY

TINCA ONOFREI, VIORICA DULMAN, LUCIA ODOCHIAN and VALERIU ȘUNEL

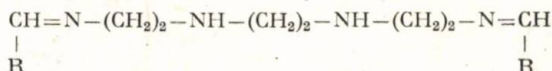
## 1. Introduction

Triethylenetetramine (TRIEN), used in syntheses in chemical industry, can be determined by titrimetric [1] ... [3], colorimetric and nephelometric methods [4] ... [7] and gravimetrically with salicylic aldehyde [8].

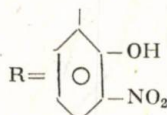
In order to analyse the technical products and the solutions in which TRIEN is to be found in a high concentration we have investigated the possibility of extending the gravimetric methods. Three methods of gravimetric analysis have been worked out using as precipitating agents derivatives of salicylic aldehyde. In contrast with the method previously described [8] we have obtained crystalline precipitates that could easily be filtered and that do not adhere to the walls of the beaker.

## 2. Experimental, Results and Discussions

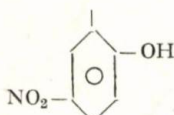
The methods of gravimetric determination we have worked out are based on the precipitating reaction between TRIEN and 3-nitro-, 5-nitro- and 5-chlorinesalicylaldehyde with the formation of Schiff bases:



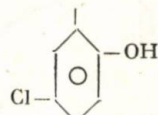
where



Compound I



Compound II



Compound III

The precipitating forms have been characterized by elementary, thermogravimetric analysis and by IR spectra.

The structure of precipitates I, II and III has been determined on the basis of elementary analyses (Table 1) and of IR spectra.

From the analysis of IR spectra there results the appearance of an absorption maximum at  $1620 \text{ cm}^{-1}$  attributed to C=N group, a band at  $1135\text{--}1140 \text{ cm}^{-1}$  for C—N and the absence of the signal corresponding to the vibration

**Table 1**  
*Analytic Data of Precipitating Forms*

| Compound   | Formula                  | C, [%] |       | H, [%] |       | Cl, [%] |       | N, [%] |       |
|------------|--------------------------|--------|-------|--------|-------|---------|-------|--------|-------|
|            |                          | Calc.  | Found | Calc.  | Found | Calc.   | Found | Calc.  | Found |
| <i>I</i>   | $C_{20}H_{24}N_6O_6$     | 54.05  | 54.58 | 5.40   | 5.82  | —       | —     | 14.41  | 14.79 |
| <i>II</i>  | $C_{20}H_{24}N_6O_6$     | 54.05  | 54.63 | 5.40   | 5.95  | —       | —     | 14.41  | 14.90 |
| <i>III</i> | $C_{20}H_{24}Cl_2N_4O_2$ | 56.73  | 57.60 | 5.67   | 6.65  | 16.78   | 17.52 | 13.23  | 14.15 |

of the C=O group from the initial molecules of salicylaldehydes, which confirms their condensation with TRIEN.

The thermograms have been registered in the air under nonisothermic conditions at a heating rate of 12°C/min using a MOM—Budapest derivatograph.

From the thermogram of compound *I* (Fig. 1) there follows that the degradation occurs in three well separated stages up to 300°C, the second stage, the most important one, being accompanied by a strong exothermic effect.

The thermograms of compounds *II* and *III* (Fig. 2) point out three

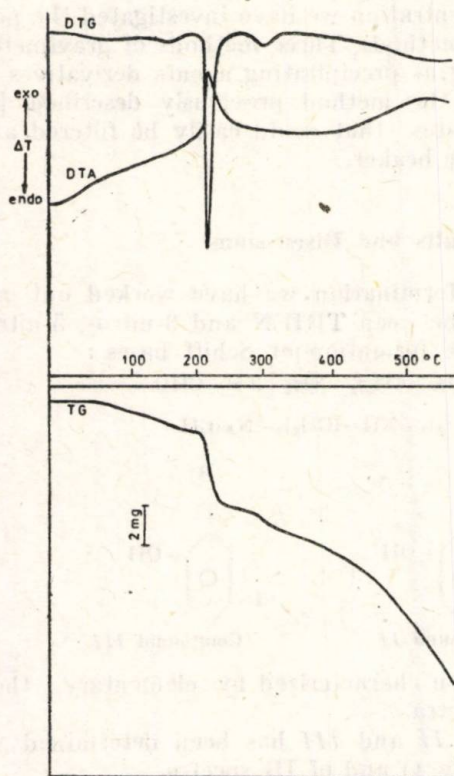


Fig. 1. — DTG, DTA and TG curves of compound *I*.

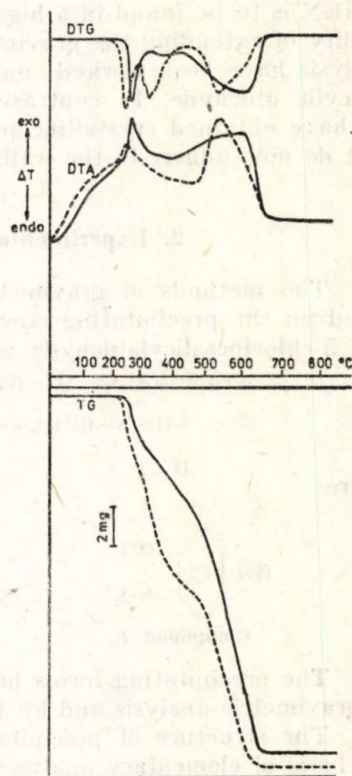


Fig. 2. — DTG, DTA and TG curves: — compound *II*; — — — compound *III*.



stages of decomposition up to 660°C, the last one being significant (exothermic effect).

The thermostability of the precipitating forms was determined on the basis of the initial decomposing temperatures (Table 2), of the temperatures

Table 2

*The Characteristic Temperatures for the First Stage*

| Compound | $T_i$ , [°C] | $T_m$ , [°C] | $T_f$ , [°C] |
|----------|--------------|--------------|--------------|
| I        | 45           | 154          | 195          |
| II       | 227          | 263          | 321          |
| III      | 177          | 258          | 296          |

at low transformation degrees (Fig. 3) and of the activating energies calculated by Freeman-Carroll method [9] for first stage (Table 3). The

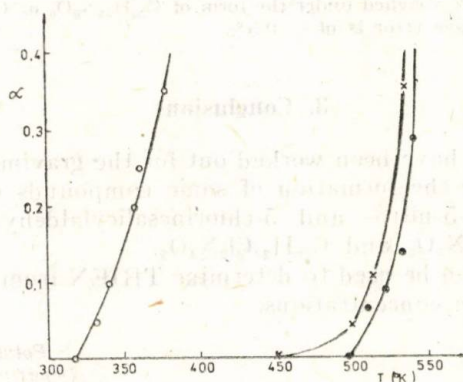


Fig. 3.— The transformation degree dependence on temperature: o—compound I; ●—compound II; x—compound III.

Table 3

*The Kinetic Parameters*

| Compound | Stage I |                  | Stage II |                  | Stage III |                  |
|----------|---------|------------------|----------|------------------|-----------|------------------|
|          | $n$     | $E_a$ , [Kj/mol] | $n$      | $E_a$ , [Kj/mol] | $n$       | $E_a$ , [Kj/mol] |
| I        | —       | —                | 0        | 432.32           | 1.4       | 339.68           |
| II       | 5       | 459.5            | —        | —                | —         | 252.4            |
| III      | 0.5     | 199.4            | 2        | 333.3            | —         | 110.1            |
|          |         |                  |          |                  | —         | 287.2            |
|          |         |                  |          |                  | —         | 120.9            |

results we have obtained lead to the conclusion that the thermic stability follows the order :

compound *II* > compound *III* > compound *I*.

Compound *I* is stable up to 45°C, compound *II* up to 227°C and compound *III* up to 177°C. Having in view the low thermostability of compound *I*, in contrast with compounds *II* and *III*, it cannot be brought to a constant mass in gravimetric determination by heating.

### 2.1. Procedure

The solution containing 0.1...0.15 g TRIEN is diluted with 70...75 cm<sup>3</sup> distilled water and is treated with a solution of 3-nitro-, 5-nitro- or 5-chlorinesalicylaldehyde (0.4...0.5 g aldehyde, 10 cm<sup>3</sup> distilled water and 0.25 g NaOH) under constant stirring. It is let to rest for 30 min. and pH is corrected at 8.3 with H<sub>2</sub>SO<sub>4</sub> 27% and 0.1 N in the presence of phenolphthaleine (alcoholic solution 0.1%) and with universal indicator paper, after which it is let to rest for an hour. An equal volume of ethylic alcohol (100 cm<sup>3</sup>) is added. The precipitate remains in contact with the solution for 5...24 hours and then it is filtered through a G<sub>4</sub> crucible. The washing is done with a C<sub>2</sub>H<sub>5</sub>-OH-H<sub>2</sub>O solution (1 : 1 v/v).

Compound *I* is orange in colour. It is dried for about two hours in vacuum desiccator and is weight as C<sub>20</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub>.

Compounds *II* and *III* are dried for about two hours at 100°C. The precipitates are yellow in colour. They are weighed under the form of C<sub>20</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub> or C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>.

The relative average error is of ± 0.5%.

### 3. Conclusions

Three methods have been worked out for the gravimetric determination of TRIEN based on the formation of some compounds of the Schiff bases type with 3-nitro-, 5-nitro- and 5-chlorinesalicylaldehyde. The forms of weighing are C<sub>20</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub> and C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>.

The methods can be used to determine TRIEN from technical products and solutions of high concentrations.

Received, July 30, 1987

Polytechnic Institute, Jassy,  
Department of Inorganic and  
Analytical Chemistry  
and  
Department of Organic and  
Macromolecular Chemistry and  
Technology

### REFERENCES

1. Bellen Z., Chem. Analit. (Warszawa), **11**, 57 (1966).
2. Bellen Z., Chem. Analit. (Warszawa), **11**, 1011 (1966).
3. Fișel S., Ungurenașu-Onofrei T., Dulman V., Rev. Chim. (București), **32**, 483 (1981).
4. Zaleski I., Chojnicka B., Roczn. panst. Zakl. Hig., **16**, 171 (1965).
5. Chojnicka B., Roczn. panst. Zakl. Hig., **16**, 477 (1965).
6. Chojnicka B., Roczn. panst. Zakl. Hig., **16**, 545 (1965).
7. Омельянец Н. И., Лаб. Дело, 483 (1966).
8. Fișel S., Ungurenașu-Onofrei T., Dulman V., Rev. Chim. (București), **31**, 585 (1980).
9. Freeman E. S., Carroll B., J. Phys. Chem., **62**, 394 (1958).



## DETERMINAREA GRAVIMETRICĂ A TRIETILENTETRAAMINEI

(Rezumat)

S-au elaborat trei metode de determinare gravimetrică a trietilentetraaminei (TRIEN) bazate pe formarea unor compuși de tip baze Schiff cu 3-nitro-, 5-nitro- și 5-clorsalicilaldehida. Precipitatele obținute au fost caracterizate prin analiză elementară, termogravimetrică și spectre IR.

Formele de cîntărire sînt  $C_{26}H_{24}N_6O_6$  și  $C_{26}H_{24}Cl_2N_4O_2$ . Eroarea medie relativă este de  $\pm 0,5\%$ .

Metodele se pot folosi pentru determinarea TRIEN din produse tehnice și soluții cu concentrații mari.

## DETERMINING QUALITY OF A THERMAL SPRING

(Continued)

When a spring is found to be of the thermal type, the first step is to determine its temperature. This is done by using a thermometer of the type known as a "maximum and minimum" thermometer. This type of thermometer is so constructed that it will record the highest and lowest temperatures to which it is subjected. It is used in the following manner: The thermometer is placed in the spring and left for a sufficient length of time to allow it to become acclimated to the temperature of the water. The thermometer is then removed and the temperature is read. The thermometer is then placed in the spring again and left for a sufficient length of time to allow it to become acclimated to the temperature of the water. The thermometer is then removed and the temperature is read. This process is repeated until a sufficient number of readings have been obtained to determine the average temperature of the spring.



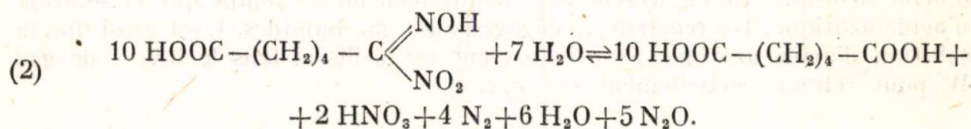
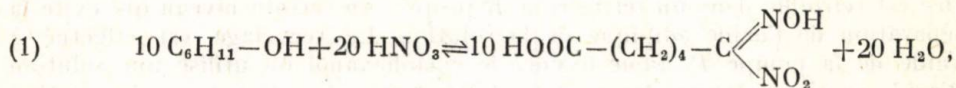
LE MODÈLE MATHÉMATIQUE DE L'INSTALLATION DE  
FABRICATION DE L'ACIDE ADIPIQUE (I)

PAR

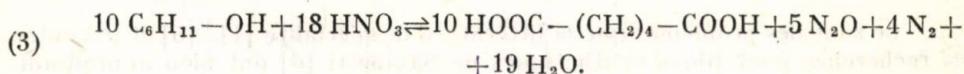
I. CURIEVICI, VIORICA NICU, ȘT. UNGUREANU, CORNELIU PETRILĂ,  
RODICA DIACONESCU, M. NICU, ELENA IONESCU et SAVEL MATACHE

## 1. Présentation de l'installation modélée

Dans le travail ci-présent on élabore le modèle mathématique d'une installation industrielle pour la fabrication de l'acide adipique à partir du cyclohexanol dont l'oxydation catalytique (métavanadate d'ammonium et sels de cuivre) se produit en deux étapes, avec acide azotique, conformément aux réactions :



La réaction globale est donc :



Le schéma de principe d'une telle installation est présenté dans la Fig. 1. Comme on peut y voir, l'installation présente deux cycles successifs : pendant le premier on réalise la transformation la plus poussée possible du cyclohexanol en acide nitrolique et la transformation partielle de celui-ci en acide adipique ; pendant le deuxième cycle a lieu la transformation complète du cyclohexanol en acide nitrolique et puis la transformation de ce dernier en acide adipique.

Le premier cycle est justifié par la nécessité de maintenir la température du réacteur à un niveau relativement réduit (la réaction globale est largement exothermique), ce qu'on peut réaliser en recyclant intensivement la masse réactionnelle refroidie après sa sortie du réacteur. Ce refroidissement est précédé par la séparation et l'envoi vers le deuxième cycle d'une fraction



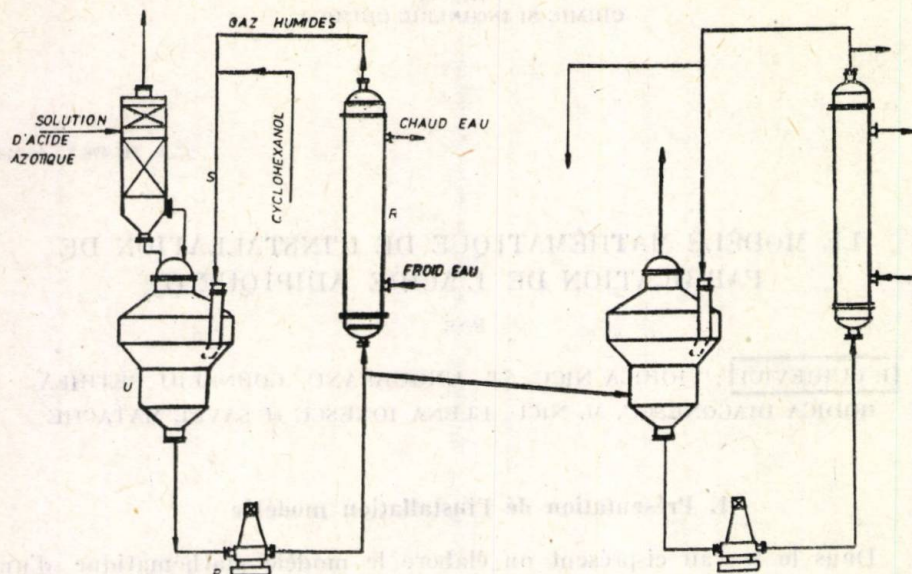


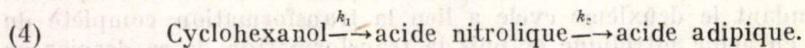
Fig. 1. — Schéma de principe de l'installation de fabrication de l'acide adipique.

qui correspond aux réactants frais introduits dans le système. La masse recyclée est refroidie dans un réfrigérant  $R$  jusqu'à un certain niveau qui évite la séparation de l'acide adipique de la solution. Le recyclage est effectué à l'aide de la pompe  $P$ . Pour oxyder le cyclohexanol on utilise une solution d'acide azotique. Le catalyseur est introduit en même temps que la solution d'acide azotique. Du réacteur se dégagent des gaz humides. C'est ainsi que la solution d'acide azotique avec catalyseur est utilisée dans le laveur de gaz  $W$  pour retenir partiellement ces gaz.

## 2. Cinétique et thermodynamique du processus

Ce sont des problèmes que la littérature de spécialité [1]...[5] et le Centre de recherches pour fibres synthétiques de Săvinești [6] ont bien approfondi.

Du point de vue cinétique le processus de formation de l'acide adipique, par oxydation avec acide azotique, en présence des catalyseurs ci-dessus mentionnés, à une température ne dépassant pas  $60^{\circ}\text{C}$  environ, est une réaction consécutive ayant la forme :



En notant par  $C_{A_0}$  la concentration molaire totale de substance organique dans la masse réactionnelle à un certain moment  $\tau$  et par  $X$ ,  $Y$ ,  $Z$  les fractions molaires du cyclohexanol et respectivement de l'acide nitrolique et adipique en phase organique, il résulte que :

$$(5) \quad C_{A_0} = C_{A_0}X + C_{A_0}Y + C_{A_0}Z.$$



Dans les travaux [1]...[4] on met en évidence que la réaction de formation de l'acide nitrolique est de premier ordre par rapport au cyclohexanol et donc :

$$(6) \quad r_A = - \frac{dC_{A_0}X}{d\tau} = -k_1 C_{A_0}X.$$

En intégrant l'équation (6), dont la condition initiale est  $X=1$  pour  $\tau=0$ , on obtient, pour la fonction du variation en temps de la concentration du cyclohexanol, l'expression :

$$(7) \quad X = e^{-k_1\tau}.$$

La réaction selon laquelle l'acide nitrolique passe en acide adipique est également de I-er ordre et par conséquent :

$$(8) \quad r_B = \frac{dC_{A_0}Y}{d\tau} = C_{A_0}(k_1X - k_2Y).$$

En intégrant l'équation (8), dont la condition initiale est  $Y=0$  pour  $\tau=0$ , on obtient, pour la variation de la concentration de l'acide nitrolique :

$$(9) \quad Y = \frac{k_1}{k_2 - k_1} (e^{-k_1\tau} - e^{-k_2\tau}) \quad \text{et} \quad (10) \quad \frac{dZ}{d\tau} = k_2Y.$$

Si la condition initiale est  $Z=0$  pour  $\tau=0$ , la concentration de l'acide adipique est :

$$(11) \quad Z = 1 - \frac{k_2}{k_2 - k_1} e^{-k_1\tau} + \frac{k_1}{k_2 - k_1} e^{-k_2\tau}.$$

La variation des constantes de vitesse  $k_1$  et  $k_2$  en fonction de la température est du type Arrhenius et a la forme [6] :

$$(12) \quad k_1^T = 2,9245 \cdot 10^9 e^{-\frac{7976,84}{T}}$$

et respectivement

$$(13) \quad k_2^T = 1,0145 \cdot 10^{10} e^{-\frac{9562,15}{T}}.$$

Les deux réactions sont exothermiques [6], à savoir :

$$(14) \quad \Delta H_{R_1}^{298} = -195,22 \text{ Kcal/mol}, \quad (15) \quad \Delta H_{R_2}^{298} = -3,775 \text{ Kcal/mol}.$$

On ne dispose pas d'informations concernant la variation de l'effet thermique fonction de température, c'est pourquoi (comme hypothèse simplificatrice) on va la négliger.

### 3. Hypothèses de travail

Le processus situé à la base du modèle mathématique a comme point de départ quelques hypothèses fondamentales auxquelles, au long des calculs, viennent s'ajouter d'autres, d'une moindre importance.

Les hypothèses fondamentales adoptées dans l'étude effectuée sont les suivantes :



a) Le système fonctionne en régime stationnaire. Il en résulte que le débit de masse, sur la chaîne dirigée vers le cycle de l'hydrolise de l'acide adipique, doit être égal au débit total de masse au moment de l'alimentation sans le débit de masse de gaz et vapeurs, qui quittent le premier cycle par le laveur.

b) En principe, la concentration du cyclohexanol en phase organique, au point de la ramification vers le deuxième cycle, pourrait avoir n'importe quelle valeur, selon les dimensions du système de réaction du premier cycle et selon les conditions de travail. On va accorder une attention particulière à la situation où le cyclohexanol est complètement consommé au point de ramification.

c) Si l'on considère le chiffre de recyclage comme le rapport entre la masse de réaction recyclée pendant le premier cycle et la masse qu'on envoie vers le cycle d'hydrolise de l'acide nitrolique, on pourra déduire ce chiffre à condition que la température dans le réacteur *U* ne dépasse pas une limite préalablement fixée du point de vue technologique.

#### 4. Géométrie du système et caractéristiques de la batterie de travail

Les deux systèmes cycliques sont identiques du point de vue constitutif. On va considérer que chacun est formé de quatre réacteurs : a) réacteur *U* — réacteur principal ; b) réacteur *V* — représenté par le système de tuyaux reliant le réacteur *U* et l'échangeur de chaleur *y* compris l'espace offert par la pompe de recirculation *P* ; c) réacteur *R*, qui est en même temps un échangeur de chaleur ; d) réacteur *S* — les tuyaux qui relient l'échangeur de chaleur *R* et le réacteur *U*.

Vu que dans le réacteur *U* a lieu un moussage et implicitement une forte agitation naturelle, on peut le considérer soit comme un réacteur continu où le mélange est parfaitement réalisé, soit comme un réacteur où le mélange n'est réalisé que dans une certaine mesure. On va considérer les trois autres réacteurs du type au déplacement total.

#### 5. Alimentation du système

Pour calculer l'alimentation du système on part de la production annuelle d'acide adipique *P*, [t/an], et de son utilisation pendant 330 jours de l'année.

En négligeant, dans une première approximation, les pertes de masse dues aux gaz qui s'échappent du réacteur quittant le système et les pertes de rendement provoquées par les transformations incomplètes de l'acide adipique, on détermine la quantité de cyclohexanol fonction de la production, à l'aide de la relation :

$$(16) \quad F_{A_0} = \frac{P \cdot 10^3}{7\,920 \cdot 146 \cdot 3\,600}, \text{ [Kmol s}^{-1}\text{]}.$$

On va corriger cette valeur, comme on le verra ci-dessous, en évaluant les pertes de gaz humides et le rendement de la transformation du cyclohexanol en acide adipique.



L'acide azotique est introduit en rapport volumétrique  $b$ , [ $\text{m}^3$  solution d'acide azotique ayant une teneur  $C_0/\text{m}^3$  en cyclohexanol]. Le rapport molaire correspondant,  $b'$  [ $\text{mol HNO}_3/\text{mol cyclohexanol}$ ], est :

$$(17) \quad b' = b \frac{\rho_{\text{HNO}_3, C_0} C_0 M_{01}}{\rho_{01} M_{\text{HNO}_3} 100}.$$

Les débits de masse d'alimentation seront :

$$(18 \text{ a}) \quad G_{01} = F_{A_0} M_{01}, \text{ [Kg/s cyclohexanol]},$$

$$(18 \text{ b}) \quad G_{\text{HNO}_3} = b' F_{A_0} M_{\text{HNO}_3}, \text{ [Kg/s acide azotique]},$$

$$(18 \text{ c}) \quad G_{\text{eau}} = b' F_{A_0} M_{\text{HNO}_3} (100 - C_0) / C_0, \text{ [Kg/s eau]}.$$

Le débit total de masse d'alimentation de la première étape du processus  $G_0$ , sera :

$$(19) \quad G_0 = F_{A_0} \left( M_{01} + b' M_{\text{HNO}_3} + b' M_{\text{HNO}_3} \frac{100 - C_0}{C_0} \right), \text{ [Kg/s]}.$$

On considère que les matières premières présentent une pureté de 100% et que la température d'alimentation est de  $50^\circ\text{C}$ .

## 6. Calcul du chiffre de recyclage

Conformément à la définition qu'on donne dans le §3c, le chiffre de recyclage est donné par :

$$(20) \quad n_R = \frac{G_R}{G_p} = \frac{G_R}{G_{01} + G_{\text{HNO}_3}}.$$

La voie principale pour calculer le chiffre de recyclage est basée sur la température maximum admissible  $T_{\max}$  dans le réacteur. Du bilan de masse du réacteur  $U$  (en négligeant les gaz qui le quittent) il résulte :

$$(21) \quad G_R = G_U - (G_{01} + G_{\text{HNO}_3})$$

et par conséquent :

$$(22) \quad n_R = \frac{G_U}{G_{01} + G_{\text{HNO}_3}} - 1,$$

où :  $G_U$  représente le débit de masse total de substance qui passe par le réacteur  $U$  qui est calculé à l'aide la relation :

$$(23) \quad G_U = \frac{\Delta Q_U}{C_{p,am} \Delta T_U}.$$

L'augmentation de la température admissible dans le réacteur est

$$(24) \quad \Delta T_U = T_{\max} - T_{am,i}.$$

On peut calculer la température du mélange au moment de l'entrée dans le réacteur,  $T_{am,i}$ , en fonction des débits d'alimentation en cyclohexanol et

en acide azotique, du débit du mélange recyclé, des températures et des chaleurs spécifiques qui leur correspondaient avant d'avoir réalisé le mélange. Comme à ce moment  $n_R$  est inconnu, il sera évalué par itérations spécifiques, en imposant, au point de la ramification, une certaine valeur à la température du matériel recyclé ainsi qu'à d'autres grandeurs qu'on va préciser au moment opportun.

La variation de l'enthalpie de la masse réactionnelle dans le réacteur est donnée par la relation :

$$(25) \quad \Delta Q_U = Q_{U,i} - Q_{U,p},$$

cù :

$$(26) \quad Q_{U,i} = Q_{01} + Q_{\text{HNO}_3} + Q_{r,U} + Q_R,$$

$$(27) \quad Q_{01} = G_{01} C_{p,01} t_a,$$

( $G_{01}$  est donné par la relation (18 a)) et :

$$(28) \quad Q_{\text{HNO}_3} = (G_{\text{HNO}_3} + G_{\text{eau}}) C_{p,\text{HNO}_3} t_a.$$

En considérant que, dans le réacteur, le cyclohexanol ne se transforme que partiellement (dans une proportion  $m$ ) la chaleur après la réaction sera :

$$(29) \quad Q_{r,U} = \frac{m Q_r}{100},$$

où :

$$(29 \text{ a}) \quad Q_r = F_{01} \Delta H_{R_1}.$$

La quantité de chaleur qui entre en même temps que le matériel recyclé est calculée à l'aide de la relation :

$$(30) \quad Q_R = G_R C_{p,mr} T_R.$$

La quantité de chaleur perdue dans le réacteur est :

$$(31) \quad Q_{Up} = Q_{pa} + Q_g.$$

Une certaine quantité de chaleur,  $Q_{pa}$ , qui est perdue par la surface extérieure du réacteur, on peut la calculer avec la relation :

$$(32) \quad Q_{pa} = \alpha_{pa} S_{pa} (T_p - T_m).$$

Le coefficient total de transfert de chaleur par convection et rayonnement, à partir des parois du réacteur vers le milieu environnant, est donné par la relation [7] :

$$(33) \quad \alpha_{pa} = [9,74 + 0,07 (T_p - T_m)] \cdot 10^{-3}, [\text{KJ/m}^2 \cdot \text{grad}].$$

Pour évaluer l'enthalpie des gaz quittant le système on peut apprécier le débit et les compositions en les considérant comme saturés en vapeurs d'eau à la température d'évacuation. Cette évaluation doit satisfaire tant le bilan thermique que celui des matériaux du système.



en acide azotique, du débit du mélange recyclé, des températures et des chaleurs spécifiques qui leur correspondaient avant d'avoir réalisé le mélange. Comme à ce moment  $n_R$  est inconnu, il sera évalué par itérations spécifiques, en imposant, au point de la ramification, une certaine valeur à la température du matériel recyclé ainsi qu'à d'autres grandeurs qu'on va préciser au moment opportun.

La variation de l'enthalpie de la masse réactionnelle dans le réacteur est donnée par la relation :

$$(25) \quad \Delta Q_U = Q_{U,i} - Q_{U,p},$$

cù :

$$(26) \quad Q_{U,i} = Q_{01} + Q_{HNO_3} + Q_{r,U} + Q_R,$$

$$(27) \quad Q_{01} = G_{01} C_{p,01} t_a,$$

( $G_{01}$  est donné par la relation (18 a)) et :

$$(28) \quad Q_{HNO_3} = (G_{HNO_3} + G_{eau}) C_{p,HNO_3} t_a.$$

En considérant que, dans le réacteur, le cyclohexanol ne se transforme que partiellement (dans une proportion  $m$ ) la chaleur après la réaction sera :

$$(29) \quad Q_{r,U} = \frac{m Q_r}{100},$$

où :

$$(29 a) \quad Q_r = F_{01} \Delta H_{R_1}.$$

La quantité de chaleur qui entre en même temps que le matériel recyclé est calculée à l'aide de la relation :

$$(30) \quad Q_R = G_R C_{p,mr} T_R.$$

La quantité de chaleur perdue dans le réacteur est :

$$(31) \quad Q_{Up} = Q_{pa} + Q_g.$$

Une certaine quantité de chaleur,  $Q_{pa}$ , qui est perdue par la surface extérieure du réacteur, on peut la calculer avec la relation :

$$(32) \quad Q_{pa} = \alpha_{pa} S_{pa} (T_p - T_m).$$

Le coefficient total de transfert de chaleur par convection et rayonnement, à partir des parois du réacteur vers le milieu environnant, est donné par la relation [7] :

$$(33) \quad \alpha_{pa} = [9,74 + 0,07 (T_p - T_m)] \cdot 10^{-3}, \text{ [KJ/m}^2 \cdot \text{grad]}.$$

Pour évaluer l'enthalpie des gaz quittant le système on peut apprécier le débit et les compositions en les considérant comme saturés en vapeurs d'eau à la température d'évacuation. Cette évaluation doit satisfaire tant le bilan thermique que celui des matériaux du système.



## Notations

- $b$  — rapport volumétrique acide azotique : cyclohexanol, dans l'alimentation,  $[m^3/m^3]$  ;  
 $b'$  — rapport molaire acide azotique : cyclohexanol ;  
 $C_{A_0}$  — concentration molaire totale de phase organique,  $[Kmol/m^3]$  ;  
 $C_0$  — concentration de la solution d'acide azotique utilisée pour alimenter l'installation,  $[\%]$  ;  
 $C_p$  — chaleur spécifique pour pression constante,  $[KJ/Kg. \text{grd}]$  ;  
 $C_{p,am}$  — chaleur spécifique du mélange réactionnel du réacteur  $U$ ,  $[KJ/Kg. \text{grd}]$  ;  
 $C_{p,01}$  — chaleur spécifique du cyclohexanol au moment de l'alimentation,  $[KJ/Kg. \text{grd}]$  ;  
 $C_{p,mr}$  — chaleur spécifique de la masse réactionnelle recirculée,  $[KJ/Kg. \text{grd}]$  ;  
 $F_{A^0}$  — débit molaire d'alimentation en cyclohexanol,  $[Kmol/s]$  ;  
 $G_0$  — débit de masse total d'alimentation,  $[Kg/s]$  ;  
 $G_{01}$  — débit de masse d'alimentation de l'installation en cyclohexanol,  $[kg/s]$  ;  
 $G_{HNO_3}$  — débit de masse d'alimentation en acide azotique,  $[Kg/s]$  ;  
 $G_{eau}$  — débit de masse d'alimentation en eau,  $[Kg/s]$  ;  
 $G_R$  — débit de masse recirculée,  $[Kg/s]$  ;  
 $G_p$  — débit de masse du produit quittant la première étape,  $[Kg/s]$  ;  
 $G_U$  — débit total de masse du mélange réactionnel qui passe par le réacteur  $U$ ,  $[Kg/s]$  ;  
 $\Delta H_{R_1}, \Delta H_{R_2}$  — effet thermique de la réaction pendant la première et respectivement la seconde étape,  $[KJ/Kmol]$  ;  
 $k_1, k_2$  — constantes des vitesses de réaction pendant la première et la seconde étape de la réaction ;  
 $m$  — quantité de cyclohexanol transformé,  $[\%]$  ;  
 $M_{01}, M_{HNO_3}$  — masses moléculaires du cyclohexanol et respectivement de l'acide azotique,  $[Kg/Kmol]$  ;  
 $n_R$  — chiffre de recyclage,  
 $p$  — production annuelle d'acide adipique,  $[t/an]$  ;  
 $Q$  — quantité de chaleur,  $[KW]$  ;  
 $Q_g$  — quantité de chaleur contenue par les gaz quittant le système,  $[KW]$  ;  
 $Q_{HNO_3}$  — quantité de chaleur de la solution d'acide azotique de l'alimentation,  $[KW]$  ;  
 $Q_{01}$  — quantité de chaleur du cyclohexanol introduit par l'alimentation de l'installation,  $[KW]$  ;  
 $Q_{pa}$  — quantité de chaleur perdue par la surface extérieure du réacteur,  $[KW]$  ;  
 $Q_r$  — quantité de chaleur obtenue après la réaction par transformation complète du cyclohexanol,  $[KW]$  ;  
 $Q_R$  — quantité de chaleur entrée en même temps que le matériel recirculé,  $[KW]$  ;  
 $Q_{r,n}$  — quantité de chaleur obtenue après la réaction par transformation d'une fraction  $m$  de cyclohexanol,  $[KW]$  ;  
 $Q_{U,p}$  — quantité de chaleur perdue dans le réacteur  $U$ ,  $[KW]$  ;  
 $\Delta Q_U$  — variation de l'enthalpie du mélange réactionnel dans le réacteur  $U$ ,  $[KW]$  ;  
 $r_A$  — vitesse de réaction par rapport au cyclohexanol,  $[Kmol/m^3 \cdot s]$  ;  
 $r_B$  — vitesse de réaction par rapport à l'acide nitrolique,  $[Kmol/m^3 \cdot s]$  ;  
 $S_U$  — surface extérieure du réacteur  $U$ ,  $[m^2]$  ;  
 $t_a$  — température des composants au moment de l'alimentation de l'installation,  $[^\circ C]$  ;  
 $T$  — température,  $[^\circ C]$  ;  
 $T_{max}$  — température maximum admissible dans le réacteur  $U$ ,  $[^\circ C]$  ;  
 $T_{am,t}$  — température de la masse réactionnelle au moment de l'entrée dans le réacteur,  $[^\circ C]$  ;  
 $T_m$  — température moyenne annuelle de l'air environnant,  $[^\circ C]$  ;  
 $T_p$  — température des parois de l'installation,  $[^\circ C]$  ;  
 $T_R$  — température du mélange recirculé,  $[^\circ C]$  ;  
 $\Delta T_U$  — augmentation admissible de la température dans le réacteur  $U$ ,  $[^\circ C]$  ;  
 $X$  — fraction molaire du cyclohexanol en phase organique ;  
 $Y$  — fraction molaire de l'acide nitrolique en phase organique ;  
 $Z$  — fraction molaire de l'acide adipique en phase organique ;  
 $\alpha_{pa}$  — coefficient de transfert de chaleur entre les parois des tuyaux et le milieu environnant,  $[KJ/m^2 \cdot \text{grd}]$  ;



$\rho_{\text{HNO}_2, C_0}$  — densité de la solution d'acide azotique de concentration  $C_0$  ;  
 $\tau$  — durée, [s].

Reçue le 11 mai 1987

Institut Polytechnique, Jassy,  
 Chaire de Génie Chimique

## BIBLIOGRAPHIE

1. Van Asselt W. J., Van Krevelan D. W., Rec. trav. chim., **82**, 1, 51 (1963).
2. Van Asselt W. J., Van Krevelan D. W., Rec. trav. chim., **82**, 5, 429 (1963).
3. Van Asselt W. J., Van Krevelan D. W., Chem. Eng. Sci., **18**, 8, 471 (1963).
4. Лубяницкий И. и сотр., Хим. Пром., 7, 529 (1960).
5. Лубяницкий И. и сотр., ЖФХ, **36**, 3, 567 (1962).
6. Matache S. et al., *Fabricarea acidului adipic*, Săvinești, 1971.
7. Pavlov K. F. et al., *Procese și aparate în ingineria chimică*, (traduit du russe). Ed. Tehn., București, 1981.

## MODELUL MATEMATIC AL INSTALAȚIEI DE FABRICARE A ACIDULUI ADIPIIC (I)

(Rezumat)

În vederea modelării matematice a instalației de fabricare a acidului adipic prin oxidarea ciclohexanolului cu acid azotic — proces continuu și ciclic — se consideră că fiecare din cele două sisteme ciclice este constituit din patru reactoare în serie. Prima parte a lucrării prezintă ipotezele de lucru în stabilirea modelului precum și datele necesare modelării: cinetica și termodinamica procesului, geometria sistemului, date asupra alimentării sistemului și calculul cifrei de reciclare.



## LE MODÈLE MATHÉMATIQUE DE L'INSTALLATION DE FABRICATION DE L'ACIDE ADIPIQUE (II)

PAR

**I. CURIEVICI**, VIORICA NICU, CORNELIU PETRILĂ, ȘT. UNGUREANU, RODICA  
DIACONESCU, M. NICU, ELENA IONESCU et SAVEL MATACHE

### 1. Élaboration du modèle mathématique pour le premier cycle

Le système d'équations décrivant la première étape de réaction part du point de ramification vers la deuxième étape, respectivement de la ramification de la masse recyclée vers l'échangeur de chaleur  $R$  [1].

Vu que le débit de masse sur le tuyau se dirigeant vers la deuxième étape doit être égal à celui d'alimentation du système sans tenir compte du débit des gaz saturés en vapeurs d'eau, le débit peut être immédiatement calculé sur cette ramification. Compte tenu du chiffre de recirculation, il résulte qu'on peut également calculer le débit de masse sur l'échangeur de chaleur. Quant aux compositions de ces deux courants, elles sont évidemment identiques au point de la ramification, mais elles sont établies selon la structure dimensionnelle et les conditions de travail de la première étape. En considérant pour l'instant tant la structure dimensionnelle que les conditions de travail comme des variables disponibles, on peut analyser la composition au point de ramification, dans deux hypothèses :

a) Au point de ramification, la quantité de cyclohexanol est entièrement transformée en acide nitrolique.

b) Ce n'est qu'une fraction quelconque de cyclohexanol qui se transforme en acide nitrolique.

On vérifie ensuite, par des essais successifs, si les régimes réalisés dans les hypothèses ci-dessus peuvent conduire au régime stationnaire supposé au début du processus.

#### 1.1. Calcul de la composition, au point de ramification, dans l'hypothèse de la transformation complète du cyclohexanol

En considérant les fuites de gaz comme une fraction  $\epsilon (\ll 1)$  du débit d'alimentation du système en cyclohexanol, à l'aide du bilan de masse globale du système on obtient :

$$(1) \quad P = G_{01}(1 - \epsilon) \frac{M_{\text{ac. adipique}}}{M_{01}}.$$



Ayant également en vue le rendement du processus, la production d'acide adipique sera :

$$(2) \quad P = \eta G_{01}(1 - \varepsilon) \frac{M_{ac. adipique}}{M_{01}}.$$

Avec la valeur du débit de masse du cyclohexanol obtenue par cette voie et à partir des relations (18), (19) [1] on peut calculer le débit total de masse d'alimentation  $G_0$  de la première étape du processus. En utilisant la relation (20) [1] il résulte que le débit de masse du mélange réactionnel à recycler sera :

$$(3) \quad G_R = n_R G_0.$$

Compte tenu que  $G_0$  est donné par la relation (19) [1] il résulte que :

$$(4) \quad F_{AR} = n_R F_{A_0}.$$

En considérant que  $\rho_{am}$  représente la densité de la masse réactionnelle du système, le débit volumétrique de masse réactionnelle sera  $G_R/\rho_{am}$  et par conséquent la concentration de la masse réactionnelle en phase organique, dans le circuit de recyclage, sera :

$$(5) \quad C_{A_0} = \frac{F_{AR} \rho_{am}}{G_R} = \frac{F_{A_0}}{G_0} \rho_{am}.$$

Dans l'hypothèse de la consommation complète du cyclohexanol au point de la ramification :

$$(6) \quad Y + Z = 1.$$

La fraction molaire de l'acide nitrolique en phase organique au point de la ramification découle de la cinétique de réaction. De l'équation (8) [1] il résulte que la fraction molaire de l'acide nitrolique atteint sa valeur maxima à :

$$(7) \quad \tau_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2} \quad \text{et} \quad (8) \quad Y_{\max} = \left(\frac{k_2}{k_1}\right)^{k_2/(k_1 - k_2)}.$$

Les constantes de vitesse fonction de température sont données par les expressions (12) et (13) [1].

Les fractions molaires d'acide nitrolique et adipique en phase organique, ainsi que la concentration de ce dernier étant connues, on peut déterminer la concentration de ces deux composants. À l'aide de la consommation complète du cyclohexanol on peut calculer, du point de vue stoechiométrique, la consommation d'acide azotique et donc la teneur de la masse réactionnelle en acide azotique.

#### 1.2. Calcul de la composition au point de ramification dans l'hypothèse de la transformation partielle du cyclohexanol

Soit  $1 > x > 0$  la fraction molaire du cyclohexanol en phase organique au point de ramification. De la vitesse de réaction de la première étape (équation (6) [1]) on peut déterminer la durée de réaction. À l'aide de l'équation (11)



[1] on détermine ensuite la fraction molaire de l'acide adipique. X et Z étant déterminés, on peut calculer la fraction molaire de l'acide nitrolique à partir de l'équation (9) [1]. Les autres grandeurs qui décrivent la composition sont calculées tout comme dans le § 1.

## 2. Équations de bilan sur l'échangeur de chaleur

Soit  $T_{R_0}$  la température de la masse réactionnelle recyclée au moment où elle entre dans l'échangeur de chaleur et soit  $\Delta T_R$  la chute maximum admissible de la température de la masse réactionnelle le long (des tubes) de l'échangeur de chaleur.

C'est l'acide nitrolique qui est le composant dont on suit l'évolution. En poursuivant la variation de sa concentration en phase organique on suit implicitement la variation de la concentration du cyclohexanol et de l'acide nitrolique.

Le calcul sera dirigé d'une manière générale, respectivement pour une concentration quelconque de l'acide nitrolique  $C_A$ ,  $Y_R(l)$ , où  $l$  représente la distance entre les orifices d'entrée des tubes de l'échangeur et le point considéré. Le bilan différentiel de masse est :

$$(9) \quad \frac{dY_R(l)}{dl} = \frac{N\pi D_R^2}{4n_R F_{A_0}} [r_A(l) + r_B(l)].$$

On calcule la vitesse de réaction  $r_B(l)$  conformément à la relation (8) [1]. La condition initiale pour intégrer l'équation (9) est soit la valeur  $Y_{\max}$ , donnée par la relation (8) dans le cas de la première hypothèse, soit la valeur qui résulte en imposant à X une certaine valeur tout comme dans le § 1.2.

La température, en tant que fonction de  $l$ , par l'intermédiaire de la constante de la vitesse de réaction, intervient comme une inconnue. C'est pourquoi il s'avère nécessaire encore une équation différentielle qu'on peut obtenir du bilan thermique.

Pour simplifier on va supposer que la température est une fonction linéaire de  $l$ , du type :

$$(10) \quad T_R(l) = T_{R_0} - \frac{\Delta T_R l}{L_R}.$$

En tenant compte de l'effet thermique des deux réactions,  $\Delta H_{R_1}$  et  $\Delta H_{R_2}$ , et de l'échange de chaleur avec l'extérieur et en acceptant pour  $K$  une valeur constante le long des tubes de l'échangeur de chaleur, l'équation de bilan thermique intégral se présente sur la forme :

$$(11) \quad n_R G_0 C_{p,am} T_{R_0} - n_R G_0 C_{pm} \Delta T_R - K S_R \Delta T_{R_m} + \\ + N \frac{\pi D_R^2}{4} \Delta H_{R_1} \int_0^{L_R} dr_B(l) + N \frac{\pi D_R^2}{4} \Delta H_{R_2} \int_0^{L_R} dr_A(l) = 0,$$



où  $\Delta T_{R_m}$  représente la différence moyenne logarithmique de température le long des tubes de l'échangeur de chaleur et  $S_R$ —la surface totale d'échange de chaleur à l'intérieur de l'échangeur. La chaleur spécifique de la masse réactionnelle est calculée fonction de sa composition moyenne aux moments où celle-ci entre et sort de l'échangeur.

La solution simultanée des équations (9) et (11), avec les conditions à la limite correspondantes, aboutit au profil de la fraction molaire de l'acide nitrolique en phase organique et de la température le long des tubes de l'échangeur de chaleur.

### 3. Équations de bilan sur les tuyaux supérieurs

Soient, pour un cas quelconque,  $X_{R,f}$ ,  $Y_{R,f}$  et  $Z_{R,f}$  les fractions molaires respectives du cyclohexanol, de l'acide nitrolique et de l'acide adipique, au moment où elles sortent de l'échangeur. Soient encore  $D_s$  et  $L_s$  le diamètre et respectivement la longueur des tuyaux supérieurs arrivant jusqu'au réacteur.

Ayant en vue la transformation du cyclohexanol en acide nitrolique et la transformation partielle de ce dernier en acide adipique, on obtient pour le bilan différentiel de masse de l'acide nitrolique, l'équation :

$$(12) \quad F_{AR} \frac{dY_s(l)}{dl} = \frac{\pi D_s^2}{4} [r_A(l) + r_B(l)].$$

Le bilan thermique est nécessaire tout comme dans le cas de l'échangeur. Dans l'équation du bilan thermique interviennent l'effet thermique de réaction et la chaleur échangée avec l'environnement. La forme différentielle de cette équation est :

$$(13) \quad G_R C_{p, am} \frac{dT_s(l)}{dl} + \pi \alpha_{pa} D_s [T_s(l) - T_m] = \\ = \frac{\pi D_s^2}{4} [r_A(l) \Delta H_{R_1} + r_B(l) \Delta H_{R_2}],$$

avec la condition initiale :

$$(14) \quad T_{s_0} = T_{Rf}.$$

Dans l'équation ci-dessus, pour calculer la transmission de chaleur vers l'environnement on n'a pas eu en vue que la résistance thermique principale représentée par la couche d'air extérieure. Pour le coefficient  $\alpha_{pa}$  on utilise des valeurs usuelles.

L'intégration simultanée des équations (12) et (13), avec les conditions à la limite correspondantes, aboutit au profil des fractions molaires des composants en phase organique et de la température de la masse réactionnelle au long des tubes supérieurs.



#### 4. Équations de bilan sur le réacteur

Ayant en vue les conditions à l'intérieur du réacteur (dégagement puissant de gaz, température élevée) on peut, en principe, accepter qu'il s'agit d'un réacteur au mélange parfait.

On peut caractériser l'éventuel écart du mélange parfait par un coefficient empirique  $0 < \beta < 1$  appliqué aux vitesses de réaction. Vu cette possibilité, la composition à la sortie du réacteur sera calculée séparément pour le mélange parfait et respectivement pour le mélange imparfait.

Le calcul de la composition de la masse réactionnelle au moment où elle sort du réacteur sera effectué d'une manière générale et il sera ensuite particularisé pour  $\beta = 1$ .

Dans le réacteur entrent le débit de masse à recycler,  $G_R$ , dont la composition est calculée dans le § 1, ainsi que du cyclohexanol et de l'acide azotique dilué, calculées dans le § 5.

Pour la densité  $\rho_{am}$  du mélange réactionnel recyclé, les débits volumétriques des deux courants seront :

a) pour les matières premières fraîches :

$$(15) \quad Q_{V_1} = \frac{F_{A_0} 100}{\rho_{01}} + \frac{G_0 - F_{A_0} 100}{\rho_{HNO_3, C_0}}, \text{ [m}^3/\text{s]},$$

b) pour le mélange recyclé :

$$(16) \quad Q_{V_2} = \frac{n_R G_R}{\rho_{am}}, \text{ [m}^3/\text{s]},$$

le débit total en résultant :

$$(17) \quad Q_{VT} = Q_{V_1} + Q_{V_2}.$$

Le courant global d'alimentation contient comme phase organique :

$$(18 \text{ a}) \quad F_{A_0} + n_R F_{A_0} X_{sf}, \text{ [Kmol/s cyclohexanol]},$$

$$(18 \text{ b}) \quad n_R F_{A_0} Y_{sf}, \text{ [Kmol/s acide nitrolique]},$$

$$(18 \text{ c}) \quad n_R F_{A_0} (1 - X_{sf} - Y_{sf}), \text{ [Kmol/s acide adipique]}.$$

La teneur totale en phase organique de l'alimentation du réacteur est donc  $F_{A_0}(n_R + 1)$ .

Les fractions molaires des trois composants en phase organique, au moment où elles entrent dans le réacteur, seront :

$$(19 \text{ a}) \quad X_{U,0} = \frac{1}{n_R + 1}, \text{ pour le cyclohexanol};$$

$$(19 \text{ b}) \quad Y_{U,0} = \frac{n_R Y_{sf}}{n_R + 1}, \text{ pour l'acide nitrolique};$$

$$(19 \text{ c}) \quad Z_{U,0} = \frac{n_R (1 - Y_{sf})}{n_R + 1}, \text{ pour l'acide adipique}.$$



La concentration molaire totale en phase organique à l'entrée dans le réacteur est :

$$(20) \quad C_{A_0, U} = \frac{F_{A_0}(n_R+1)}{Q_{VT}}, \text{ [Kmol/m}^3\text{]}.$$

En considérant la concentration des composants à leur sortie du réacteur, ainsi que la température, comme identiques à celles qu'on trouve à l'intérieur du réacteur, même si le mélange n'est pas parfait, pour un volum  $V_U$  du réacteur le bilan intégral de masse du cyclohexanol est de la forme :

$$(21) \quad F_{A_0}(1+n_R X_{S,f}) - F_{A_0}(n_R+1) X_{U,f} - V_U r_A \beta = 0,$$

la vitesse de réaction en résultant de l'équation :

$$(22) \quad r_A = k_1 X_{U,f} \frac{F_{A_0}(n_R+1)}{Q_{VT}}.$$

Dans les mêmes hypothèses, le bilan intégral de masse de l'acide nitrolique est :

$$(23) \quad F_{A_0} n_R Y_{S,f} - F_{A_0}(n_R+1) Y_{U,f} \mp V_U \beta r_B = 0$$

et la vitesse de réaction :

$$(24) \quad r_B = \frac{F_{A_0}(n_R+1)}{Q_{VT}} (k_1 X_{U,f} - k_2 Y_{U,f}).$$

En négligeant les pertes de chaleur qui accompagnent les gaz s'échappant du réacteur, pour une surface d'échange de chaleur avec l'extérieur  $S_U$ , le bilan énergétique intégral du réacteur est :

$$(25) \quad G_0(n_R+1) C_{p,am}(T_{U,0} - T_{U,f}) + F_{A_0}(n_R+1)(X_{U,0} - X_{U,f}) \Delta R_1 + \\ + F_{A_0}(n_R+1)(Z_{u,f} - Z_{u,i}) \Delta H_{R_2} - \alpha_{p,a} S_U (T_{f,U} - T_m) = 0.$$

La solution simultanée des équations (21), (23) et (25) conduit aux valeurs des fractions molaires des composants de la masse réactionnelle du réacteur et de la température du réacteur.

## 5. Équations de bilan sur les tuyaux inférieurs

Le débit molaire de phase organique le long du trajet des tuyaux inférieurs qui relient le réacteur et l'échangeur de chaleur est  $F_{A_0}(n_R+1)$ . Les fractions molaires des trois composants — cyclohexanol, acide nitrolique et acide adipique — sont respectivement  $X_v(l)$ ,  $Y_v(l)$  et  $Z_v(l)$ .

Le débit de masse totale le long des tuyaux est  $G_0(n_R+1)$ , [Kg/s] et le débit volumétrique, pour une densité  $\rho_{am}$  de la masse réactionnelle, est :

$$(26) \quad Q_{VT} = \frac{G_0(n_R+1)}{\rho_{am}}.$$



Pour l'acide nitrolique l'équation différentielle de bilan de masse, le long du trajet des tuyaux, sera :

$$(27) \quad F_{A_0}(n_R+1) \frac{dY_V(l)}{dl} - \frac{\pi D_V^2}{4} \cdot \frac{F_{A_0}(n_R+1)}{Q_{VT}} [k_1 X_V(l) - k_2 Y_V(l)] = 0$$

et pour le cyclohexanol :

$$(28) \quad F_{A_0}(n_R+1) \frac{dX_V(l)}{dl} + \frac{\pi D_V^2}{4} \cdot \frac{F_{A_0}(n_R+1)}{Q_{VT}} k_1 X_V(l) = 0.$$

Les conditions initiales de la solution du système antérieur sont constituées par les fractions molaires des composants en phase organique et par la température de la masse réactionnelle au moment où elle sort du réacteur. L'intégration est effectuée sur la longueur  $L_e$  des tuyaux inférieurs.

## 6. Modèle mathématique de la première étape du processus

C'est l'ensemble d'équations de bilan de masse et énergétique pour les quatre parties du système considéré qui constitue son modèle mathématique à savoir : a) équations (9) et (11) ; b) équations (12) et (13) ; c) équations (21), (23), (25) ; d) équations (27), (28) et

$$(29) \quad G_0(n_R+1)C_{pm} \frac{dT_V(l)}{dl} - \frac{\pi D_V^2}{4} \cdot \frac{F_{A_0}(n_R+1)}{Q_{VT}} [k_1 X_V(l) - k_2 Y_V(l)] \Delta H_{R_2} - \frac{\pi D_V^2}{4} \cdot \frac{F_{A_0}(n_R+1)}{Q_{VT}} k_1 X_V(l) \Delta H_{R_1} + \alpha_{pa} \pi D_V [T_V(l) - T_m] = 0.$$

Les conditions initiales pour chaque réacteur sont constituées par les valeurs finales de la température et des fractions molaires du réacteur précédent.

Les interactions commencent à l'entrée dans l'échangeur de chaleur en imposant une certaine valeur à  $T_{R,0}$  et en calculant la composition selon le procédé indiqué dans le § 1.

## 7. Paramètres disponibles du modèle

Il en résulte qu'on peut considérer comme paramètres disponibles : la température à l'entrée dans l'échangeur de chaleur, la composition de la masse réactionnelle au moment où elle entre dans l'échangeur, le rapport acide azotique : cyclohexanol, le volume du contour de la réaction qui peut être particularisé pour ses différents composants et  $\beta$  — le degré qui caractérise le mélange dans le réacteur proprement-dit du système.

Par une variation adéquate des paramètres mentionnés ci-dessus il faudra aboutir, après avoir calculé le cycle entier, à une composition de



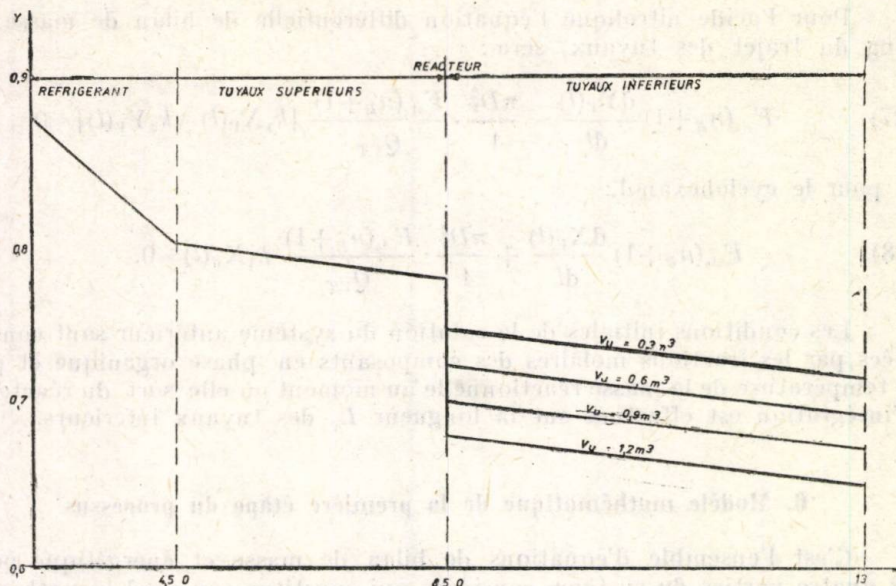


Fig. 1. — Profils des fractions molaires de l'acide nitrolrique pendant le premier cycle pour différents volumes du réacteur U.

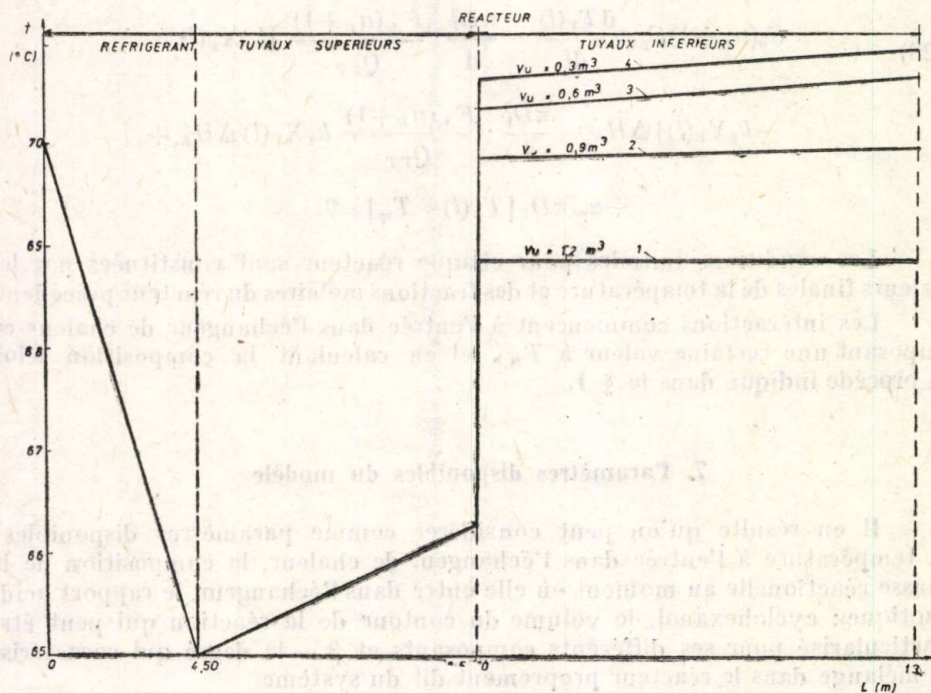


Fig. 2. — Profils de la température pendant le premier cycle pour différents volumes du réacteur U.



la masse réactionnelle et à une température d'entrée dans le réfrigérant qui soient identiques à celles qu'on avait choisies au début du calcul.

Selon ce qu'on a déjà mentionné, le calcul du cycle en entier implique des itérations successives.

Après avoir calculé le premier cycle on calcule le deuxième de la même manière pour les deux variantes, c'est-à-dire en introduisant ou non le cyclohexanol dans le cycle.

Les Fig. 1 et 2 exemplifient l'intégration du modèle mathématique avec les conditions à la limite spécifiées. L'équation de la vitesse de réaction qui se produit dans le réacteur est donnée par l'équation (6) [1].

### Notations

|                    |                                                                                                                                       |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| $C_{A^0}$          | — concentration molaire totale de phase organique, [Kmol/m <sup>3</sup> ];                                                            |
| $D$                | — diamètre, [m];                                                                                                                      |
| $D_R$              | — diamètre des tubes de l'échangeur de chaleur $R$ , [m];                                                                             |
| $D_S$              | — diamètre des tuyaux supérieurs, [m];                                                                                                |
| $D_V$              | — diamètre des tuyaux inférieurs, [m];                                                                                                |
| $F$                | — débit molaire, [Kmol/s];                                                                                                            |
| $F_{A_0}$          | — débit molaire d'alimentation de l'installation en cyclohexanol, [Kmol/s];                                                           |
| $F_{A_R}$          | — débit molaire de phase organique recirculée dans le système, [Kmol/s];                                                              |
| $G$                | — débit de masse, [Kg/s];                                                                                                             |
| $G_{01}$           | — débit de masse du cyclohexanol d'alimentation, [Kg/s];                                                                              |
| $G_R$              | — débit de masse réactionnelle recirculée, [Kg/s];                                                                                    |
| $G_0$              | — débit de masse total d'alimentation, [Kg/s];                                                                                        |
| $k_1, k_2$         | — constantes des vitesses de réaction pour la première et respectivement, la seconde étape de la réaction;                            |
| $K$                | — coefficient total de transfert de chaleur entre l'agent refroidisseur (l'eau) et la masse réactionnelle, [KJ/m <sup>2</sup> ·s·°K]; |
| $l$                | — distance courante, [m];                                                                                                             |
| $L$                | — longueur, [m];                                                                                                                      |
| $L_R$              | — longueur des tubes de l'échangeur de chaleur, [m];                                                                                  |
| $L_V$              | — longueur des tuyaux inférieurs, [m];                                                                                                |
| $M$                | — masse molaire;                                                                                                                      |
| $M_{ac. adipique}$ | — masse de l'acide adipique;                                                                                                          |
| $M_{01}$           | — masse du cyclohexanol;                                                                                                              |
| $N$                | — nombre des tubes de l'échangeur de chaleur;                                                                                         |
| $n_R$              | — chiffre de recirculation;                                                                                                           |
| $P$                | — production annuelle d'acide adipique, [t/an];                                                                                       |
| $Q_V$              | — débit volumétrique, [m <sup>3</sup> /s];                                                                                            |
| $Q_{V1}$           | — débit volumétrique pour le courant d'alimentation de l'installation, [m <sup>3</sup> /s];                                           |
| $Q_{V2}$           | — débit volumétrique pour le mélange recyclé, [m <sup>3</sup> /s];                                                                    |
| $Q_{VT}$           | — débit volumétrique total, [m <sup>3</sup> /s];                                                                                      |
| $r_A$              | — vitesse de réaction par rapport au cyclohexanol, [Kmol/m <sup>3</sup> ·s];                                                          |
| $r_B$              | — vitesse de réaction par rapport à l'acide nitrolique, [Kmol/m <sup>3</sup> ·s];                                                     |
| $S$                | — surface, [m <sup>2</sup> ];                                                                                                         |
| $S_R$              | — surface totale de transfert dans l'échangeur de chaleur $R$ , [m <sup>2</sup> ];                                                    |
| $S_U$              | — surface d'échange de chaleur avec l'extérieur du réacteur $U$ , [m <sup>2</sup> ];                                                  |
| $T$                | — température, [°K];                                                                                                                  |
| $T_m$              | — température de l'environnement, [°K];                                                                                               |
| $\Delta T_R$       | — chute maximum de température admissible le long des tubes de l'échangeur de chaleur $R$ , [°K];                                     |
| $\Delta T_{R,m}$   | — différence moyenne logarithmique de température le long des tubes de l'échangeur de chaleur, [°K];                                  |
| $V_U$              | — volume du réacteur, [m <sup>3</sup> ];                                                                                              |
| $X$                | — fraction molaire du cyclohexanol en phase organique;                                                                                |
| $Y$                | — fraction molaire de l'acide nitrolique en phase organique;                                                                          |
| $Z$                | — fraction molaire de l'acide adipique en phase organique;                                                                            |



- $\alpha_{pa}$  — coefficient de transfert de chaleur entre les parois des tubes et l'environnement,  $[KJ/m^2 \cdot s \cdot ^\circ C]$  ;  
 $\beta$  — coefficient d'écart par rapport au mélange parfait ;  
 $\Delta H_{R1}, \Delta H_{R2}$  — effet thermique de la réaction pendant la première et respectivement la deuxième étape de la réaction,  $[KJ/kmol]$  ;  
 $\epsilon$  — fraction de la fuite des gaz ;  
 $\rho$  — densité,  $[Kg/m^3]$  ;  
 $\rho_{am}$  — densité de la masse réactionnelle du système,  $[Kg/m^3]$  ;  
 $\rho_{ol}$  — densité du cyclohexanol,  $[Kg/m^3]$  ;  
 $\rho_{HNO_3}$  — densité de la solution d'acide azotique de concentration  $C_0$ ,  $[Kg/m^3]$ .

## Indices

- $R$  — échangeur de chaleur ;  
 $S$  — tuyaux supérieurs ;  
 $U$  — réacteur proprement-dit ;  
 $V$  — tuyaux inférieurs ;  
 $0$  — à l'entrée dans le réacteur correspondant ;  
 $f$  — à la sortie du réacteur correspondant.

Reçue le 11 mai 1987

Institut Polytechnique, Jassy,  
Chaire de Génie Chimique

## BIBLIOGRAPHIE

1. Curievici I. et collab., *Le modèle mathématique de l'installation de fabrication de l'acide adipique (I)*. Bul. Inst. polit. Iași, **XXX (XXXIX)**, 1-2, s. II, 35-42 (1989).
2. Curievici I., *Bazele tehnologiei chimice*. Vol. I, Inst. polit., 1981.
3. Rase H. F., *Chemical Reactor Design for Process Plants*. Vol. I, II, John Wiley & Sons, New York, 1977.
4. Mihail R., *Modelarea reactoarelor chimice*. Ed. Tehn., București, 1976.
5. Crowe C. M., *Chemical Plant Simulation*. Prentice Hall Intersc., NY, 1971.

# MODELUL MATEMATIC AL INSTALAȚIEI DE FABRICARE A ACIDULUI ADIPIC (II)

(Rezumat)

Elaborarea modelului matematic pentru primul ciclu al procesului de obținere a acidului adipic prin oxidarea ciclohexanolului începe de la punctul de ramificație spre al doilea ciclu prin calcularea compoziției pe baza datelor din prima parte a lucrării. În continuare se aplică bilanțul de masă și termic pe fiecare din cele patru zone ale sistemului. Calculul ciclului implică iterații succesive.



## EXPERIMENTAL STUDY ON HEAT TRANSFER IN THIN FILMS OF NON-NEWTONIAN LIQUIDS

BY

FĂNICĂ MUSTAȚĂ, RADU TUDOSE and ELENA COSTEA

### 1. Introduction

The heat transfer in thin film flow has numerous applications in the industrial operations such as heating, cooling, evaporation, condensation, absorption, desorption, demonomerization.

The liquid film can be formed mechanically (agitated film), gravitationally (falling film) or under the action of a gaseous phase (vapours or air) by enveloping. In spite of the large number of papers in the field, approaching the heat transfer in thin film flow of Newtonian fluids [1], [2], [4], ..., [13], there are few papers concerning the heat transfer in non-Newtonian liquid film.

J. T. Davies [3] has investigated the heat transfer in the flow of an aqueous polyacrylamide (Separan MG 200) solution, with non-Newtonian behaviour, and found a partial heat transfer coefficient lower than that of water.

The aim of this paper is to derive a correlation for partial heat transfer coefficient in thin film flow of non-Newtonian liquids.

### 2. Experimental Equipment

The main part of the experimental equipment, depicted in Fig. 1, is formed of a heat exchange tube and a circuit of thermostated hot water. The non-Newtonian liquid is set in motion by the pump (2) through the heat exchanger (3) and the flowmeter (4) and distributed by the device (5) over the external surface of the heat exchange tube (1) ( $\varnothing = 44$  mm,  $L = 2000$  mm). The heated non-Newtonian liquid is collected in the tank (6) and recycled through the heat exchanger (3) to the distribution device (5) and back to the tank (6) for regulating the flow rate and temperature.

The heating water, from the tank (7), is passed through the heater (9) by pump (8), and redistributed for regulating the flow rate and temperature at the tank (7) and then at the lower part of the heat exchange tube (1) through the flowmeter (10). The temperature of the heating water is higher than that of the non-Newtonian liquid, the heat transfer taking place in counter current, from the hot water to the liquid film.

Since the vibrations can increase the partial heat transfer coefficient up to 300% [12] the heat exchange tube was fed with the two liquids by



means of rubber tubes and the pumps have been mounted in such a way as to avoid the vibration generation.

On the external surface of the heat exchange tube, nine Copper—Constantan thermocouples have been mounted helically (Fig. 2).

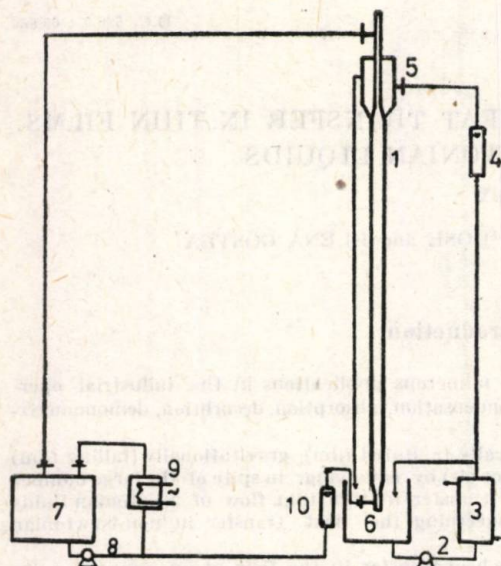


Fig. 1. — Experimental equipment: 1 — heat exchange tube; 2 — pump; 3 — heat exchanger; 4 — flowmeter; 5 — distribution device; 6 — tank; 7 — tank; 8 — pump; 9 — electric heater; 10 — flowmeter.

Though according to literature informations [12] the heat losses up to 70°C can be considered negligible and do not significantly influence the heat transfer coefficient, the heat exchange tube was protected with transparent plexiglass.

The inlet and outlet temperatures of the two fluids in the working section have been measured by means of Copper—Constantan thermocouples and Hg thermometer with an accuracy of  $\pm 0.1^\circ\text{C}$ . The temperatures at the tube and at the film surfaces have also been measured by thermocouples. To avoid some errors in measuring the temperature, the thermocouples have been made with no additional weldings.

A Dewar vessel filled with water and ice was used as zero point; the opposing electromotive force was measured by means of a Kipp a. Zonen millivoltmeter on the scales 1; 2; 5 mV.

### 3. Experimental

For determining the partial heat transfer coefficient, the temperature and flow rate of the two fluids at the input and at the output of the working zone as well as the temperatures at the external tube surface and the film surface have been measured.

Two solution of polyethyleneoxide 4 000 (provided by G.I.P. Brazi) of 46% and 56% concentration, respectively, have been used as non-Newtonian fluids. The rheological measurements have been accomplished on a Rheotest RV<sub>2</sub> — G.D.R. apparatus.

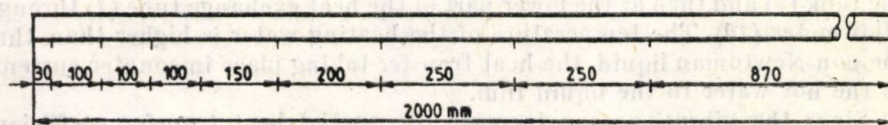


Fig. 2. — Distribution of thermocouples over the tube length.



Table 1

Variation of the Solution Densities with Temperature for the Solutions of Polyethylene Oxide 4 000

| T, [°C]                                   | 30    | 31    | 32    | 33    | 34    | 35    | 36      | 37    | 38      | 39    | 40      | 41    | 42      | 43    | 44      | 45    |
|-------------------------------------------|-------|-------|-------|-------|-------|-------|---------|-------|---------|-------|---------|-------|---------|-------|---------|-------|
| $\rho$ , [kg/m <sup>3</sup> ]<br>c = 56 % | 1 091 | 1 090 | 1 089 | 1 087 | 1 085 | 1 084 | 1 083.5 | 1 083 | 1 082.5 | 1 082 | 1 081.5 | 1 081 | 1 081   | 1 080 | 1 079.5 | 1 079 |
| $\rho$ , [kg/m <sup>3</sup> ]<br>c = 46 % | 1 070 | 1 069 | 1 068 | 1 067 | 1 065 | 1 064 | 1 063   | 1 062 | 1 061   | 1 060 | 1 059   | 1 058 | 1 057.5 | 1 057 | 1 057   | 1 056 |

Table 2

Variation of the Consistency (according of the Ostwald de Waele law) with Temperature for Solutions of Polyethylene Oxide 4 000

| T, [°C]                                             | 25    | 28    | 30    | 32    | 34    | 36    | 38    | 40    | 42    | 44     | 46    | Flow index |
|-----------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|------------|
| K, [g/cm <sup>2</sup> .s <sup>n</sup> ]<br>c = 46 % | 0.110 | 0.106 | 0.106 | 0.096 | 0.094 | 0.090 | 0.085 | 0.072 | 0.067 | 0.063  | 0.060 | 0.98       |
| K, [g/cm <sup>2</sup> .s <sup>n</sup> ]<br>c = 56 % | 0.236 | 0.204 | 0.201 | 0.168 | 0.155 | 0.194 | 0.122 | 0.108 | 0.105 | 0.1035 | 0.103 | 0.98       |



The variations with temperature of the densities of the two fluids and of the indices of consistency (according to the Ostwald—de Waele law) are showed in Tables 1 and 2, respectively.

The runs were carried out for volume flow rates between 400 and 900 l/h which correspond to  $Re$  numbers between 400 and 1720 at temperatures of the heating fluids of 45°, 50° and 60°C. The  $Re$  number was calculated by Silvester's relationship [14].

#### 4. Results and Discussion

In the flow of thin films of solutions of polyethylene oxide 4 000 the following flow zones can be noticed :

a) A smooth flow zone occurring at the upper part of the heat exchange tube which exhibit a swell immediately after the liquid leaves the distribution gap.

b) A zone of flow with periodic waves where unstable waves occur at the same points which degenerates and accumulates as drops shifting on the surface of a liquid sublayer [15], [16].

c) The transition zone where the drops have different sizes and shift at different rates which results in their coalescence and breakdown.

d) The zone of flow with stabilized waves, characterized by a narrow distribution of the drop sizes and rates, their amplitude remaining constant along the flow surface.

These zones can coexist all or only partially, function of  $Re$  value.

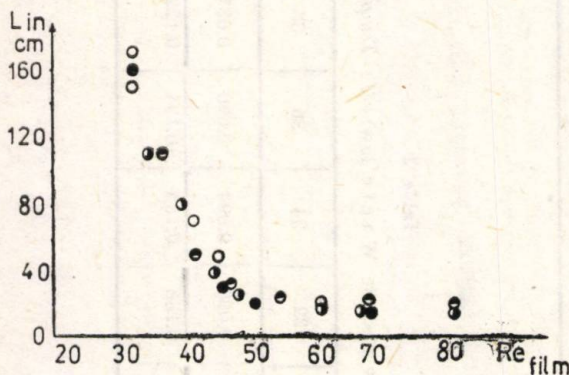


Fig. 3. — Variation of the input length vs. the  $Re$  number of the film at  $T_{inlet}=26^{\circ}C$  (○);  $T_{inlet}=40^{\circ}C$  (●);  $T_{inlet}=50^{\circ}C$  (◐);  $T_{inlet}=55^{\circ}C$  (◑).

The length of the smooth zone decreases with increasing temperatures and  $Re$  values (Fig. 3).

The partial heat transfer coefficient in the film was calculated by the relationship :

$$(1) \quad \alpha_F = K \frac{\Delta t_m}{\Delta t_M}$$

If the obtained data are worked statistically the dependence of the partial heat transfer coefficient in the film vs. the  $Re$  number values of the two fluids and the temperature of heating agent was obtained :

$$(2) \quad \alpha_F = 147.1 Re_{film}^{0.708} Re_{int}^{0.407} Qa_{film}^{-0.312}$$

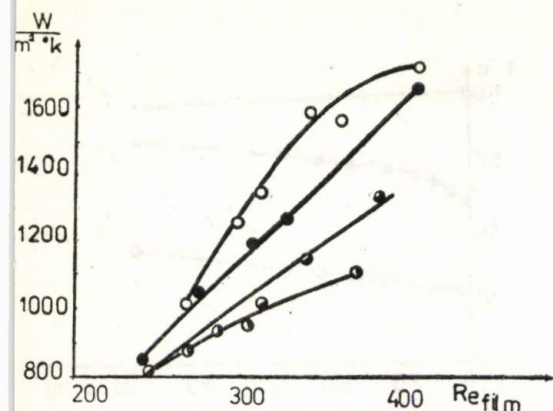


Fig. 4. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 40^\circ C$  ( $C = 56\%$ ) and  $Re_{inlet} = 7\,800$  (○);  $Re_{inlet} = 11\,000$  (●);  $Re_{inlet} = 15\,400$  (◐);  $Re_{inlet} = 18\,000$  (◑).

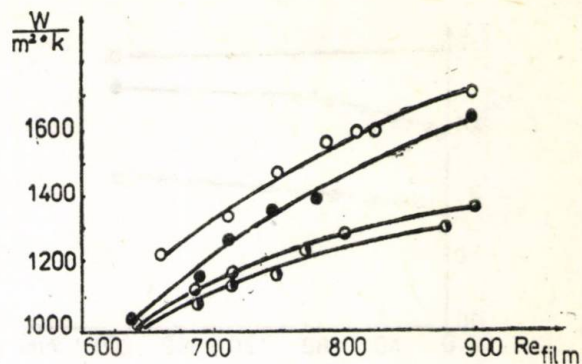


Fig. 5. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 50^\circ C$  ( $C = 56\%$ ) and  $Re_{inlet} = 7\,700$  (○);  $Re_{inlet} = 11\,000$  (●);  $Re_{inlet} = 13\,800$  (◐);  $Re_{inlet} = 19\,000$  (◑).

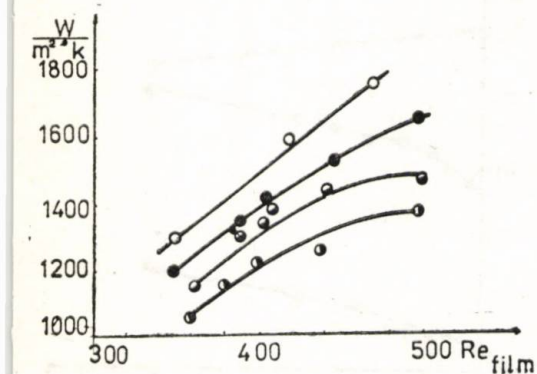


Fig. 6. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 60^\circ C$  ( $C = 56\%$ ) and  $Re_{inlet} = 7\,800$  (○);  $Re_{inlet} = 10\,800$  (●);  $Re_{inlet} = 15\,000$  (◐);  $Re_{inlet} = 19\,000$  (◑).

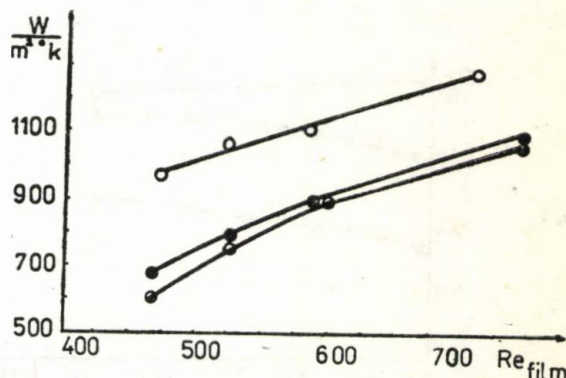


Fig. 7. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 37.5^\circ C$  ( $C = 46\%$ ) and  $Re_{inlet} = 8\,000$  (○);  $Re_{inlet} = 12\,200$  (●);  $Re_{inlet} = 17\,500$  (◐).

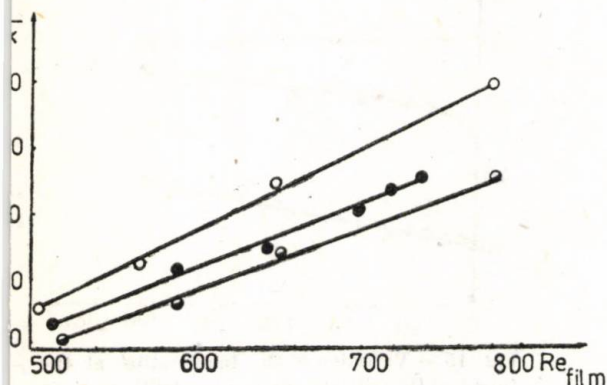


Fig. 8. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 45^\circ C$  ( $C = 46\%$ ) and  $Re_{inlet} = 7\,800$  (○);  $Re_{inlet} = 12\,600$  (●);  $Re_{inlet} = 15\,600$  (◐).

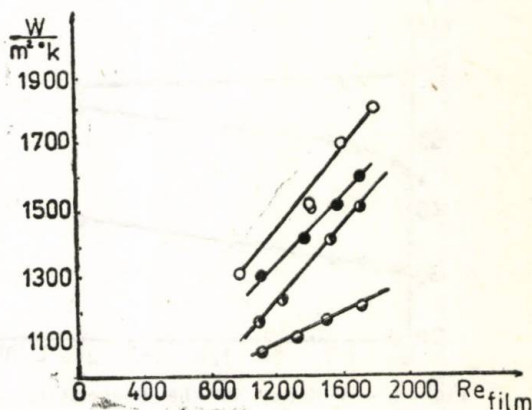


Fig. 9. — Variation of the partial heat transfer coefficient vs. the  $Re$  number of the film at  $T_{inlet} = 60^\circ C$  ( $C = 46\%$ ) and  $Re_{inlet} = 7\,700$  (○);  $Re_{inlet} = 11\,000$  (●);  $Re_{inlet} = 13\,800$  (◐);  $Re_{inlet} = 19\,000$  (◑).



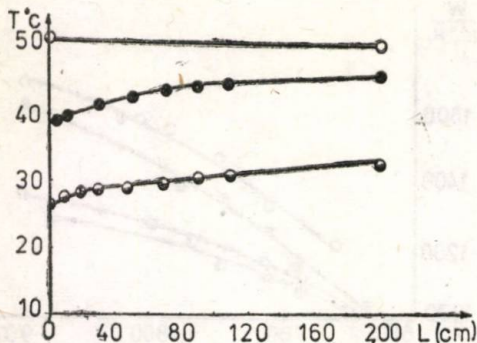


Fig. 10. — Variation of the temperature at the tube and film surfaces at  $T_{\text{inlet}} = 50^\circ\text{C}$  ( $C = 56\%$ ),  $R_{\text{inlet}} = 15\,000$ ,  $R_{\text{film}} = 540$ ; hot water (○), wall (●), film (◐).

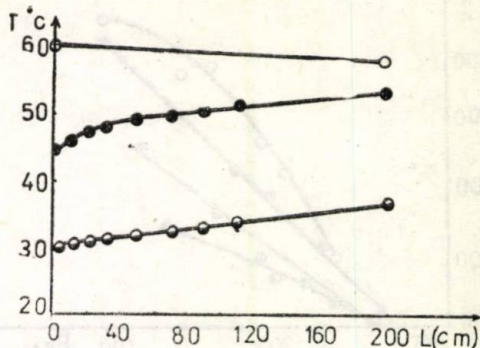


Fig. 11. — Variation of the temperature at the tube and film surfaces at  $T_{\text{inlet}} = 60^\circ\text{C}$  ( $C = 56\%$ ),  $R_{\text{film}} = 920$ ,  $R_{\text{inlet}} = 18\,000$ ; hot water (○); wall (●); film (◐).

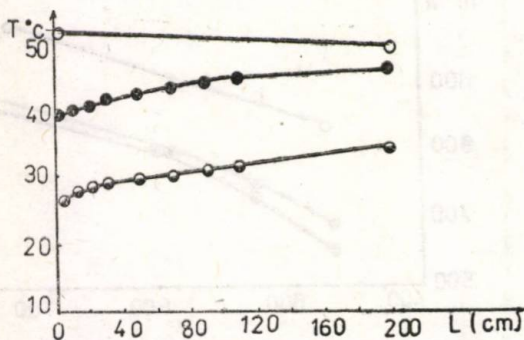


Fig. 12. — Variation of the temperature at the tube and film surface at  $T_{\text{inlet}} = 50^\circ\text{C}$  ( $C = 56\%$ ),  $R_{\text{film}} = 800$ ,  $R_{\text{inlet}} = 15\,000$ ; hot water (○), wall (●), film (◐).

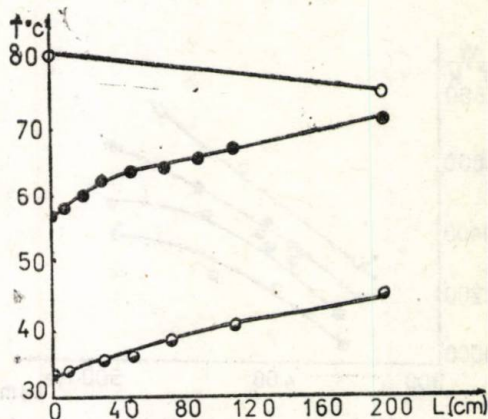


Fig. 13. — Variation of the temperature at the tube and film surfaces at  $T_{\text{inlet}} = 80^\circ\text{C}$  ( $C = 56\%$ ),  $R_{\text{film}} = 1\,040$ ,  $R_{\text{inlet}} = 15\,000$ ; hot water (○), wall (●), film (◐).

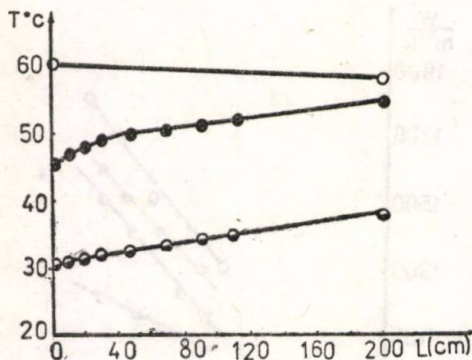


Fig. 14. — Variation of the temperature at the tube and film surface at  $T_{\text{inlet}} = 60^\circ\text{C}$  ( $C = 56\%$ ),  $R_{\text{film}} = 890$ ,  $R_{\text{inlet}} = 18\,000$ ; hot water (○), wall (●), film (◐).

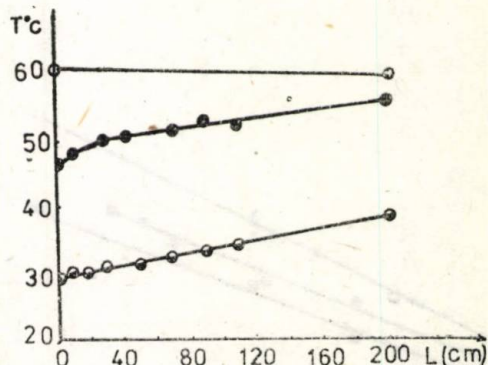


Fig. 15. — Variation of the temperature at the tube and film surface at  $T_{\text{inlet}} = 60^\circ\text{C}$ ,  $R_{\text{film}} = 890$  ( $C = 56\%$ ),  $R_{\text{inlet}} = 24\,000$ ; hot water (○), wall (●), film (◐).

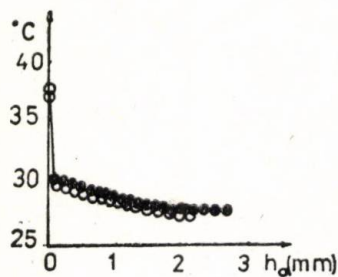


Fig. 16. — Variation of temperature vs. thickness at  $R_{s, \text{film}} = 580$ ,  $R_{s, \text{inlet}} = 18\,000$ ,  $T_{\text{film}} = 25^\circ\text{C}$ ,  $T_{\text{inlet}} = 45^\circ\text{C}$ ; length 30 mm (○), 130 mm (●);  $C = 56\%$ .

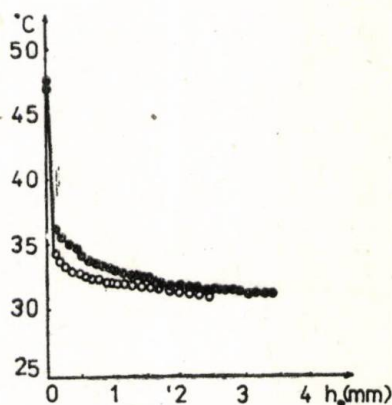


Fig. 17. — Variation of temperature vs. thickness at  $R_{s, \text{film}} = 490$ ,  $R_{s, \text{inlet}} = 18\,250$ ,  $T_{\text{film}} = 30^\circ\text{C}$ ,  $T_{\text{inlet}} = 60^\circ\text{C}$ ; length 30 mm (○), 130 mm (●);  $C = 56\%$ .

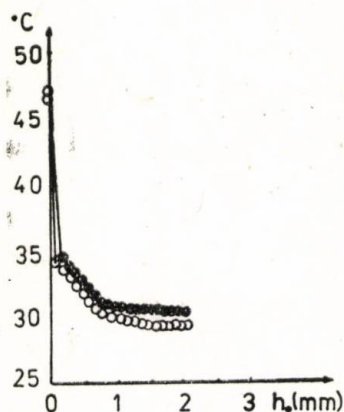


Fig. 18. — Variation of temperature vs. thickness at  $R_{s, \text{film}} = 650$ ,  $R_{s, \text{inlet}} = 18\,250$ ,  $T_{\text{film}} = 30^\circ\text{C}$ ,  $T_{\text{inlet}} = 60^\circ\text{C}$ ; length 30 mm (○), 130 mm (●);  $C = 56\%$ .

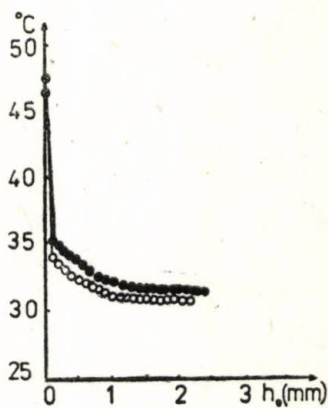


Fig. 19. — Variation of temperature vs. thickness at  $R_{s, \text{film}} = 920$ ,  $R_{s, \text{inlet}} = 18\,250$ ,  $T_{\text{film}} = 30^\circ\text{C}$ ,  $T_{\text{inlet}} = 60^\circ\text{C}$ ; length 30 mm (○), 130 mm (●);  $C = 56\%$ .



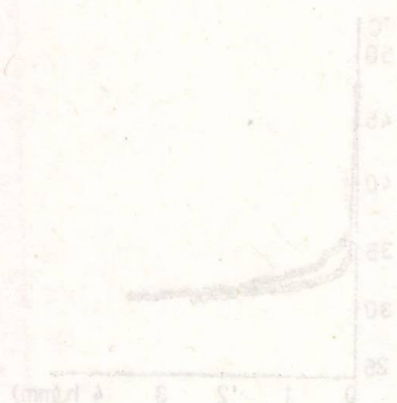


Fig. 15 - Variation of temperature vs. thickness of  $X_{\text{film}}$  = 0.20,  $K_{\text{film}}$  = 18.520,  $T_{\text{amb}}$  = 30°C,  $T_{\text{initial}}$  = 28°C, length 30 mm (○), 450 mm (●) ( $C = 20\%$ ).

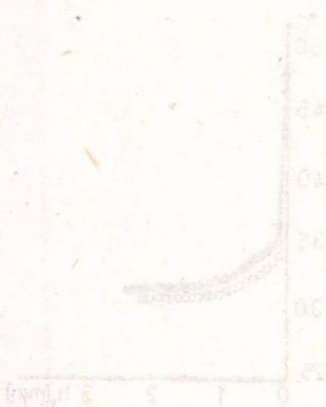


Fig. 16 - Variation of temperature vs. thickness of  $X_{\text{film}}$  = 0.20,  $K_{\text{film}}$  = 18.520,  $T_{\text{amb}}$  = 30°C,  $T_{\text{initial}}$  = 28°C, length 30 mm (○), 120 mm (●),  $C = 20\%$ .



Fig. 17 - Variation of temperature vs. thickness of  $X_{\text{film}}$  = 0.20,  $K_{\text{film}}$  = 18.520,  $T_{\text{amb}}$  = 30°C,  $T_{\text{initial}}$  = 28°C, length 30 mm (○), 120 mm (●) ( $C = 20\%$ ).

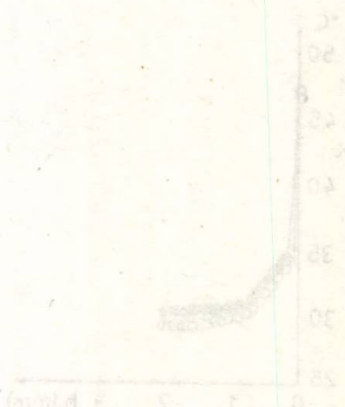


Fig. 18 - Variation of temperature vs. thickness of  $X_{\text{film}}$  = 0.20,  $K_{\text{film}}$  = 18.520,  $T_{\text{amb}}$  = 30°C,  $T_{\text{initial}}$  = 28°C, length 30 mm (○), 120 mm (●),  $C = 20\%$ .

In Figs 4...9 the variations of the partial heat transfer coefficient vs. the  $Re$  number values, at various temperatures and concentrations, as well for some  $Re$  number values of the heating fluids are plotted.

The variation of the temperature of the tube surface and of the film w.r.t. the distance to the input zone, at various  $Re$  numbers of the fluids and at various temperatures of the heating fluid, are depicted in Figs. 10...15.

The dependence of the film temperature vs. the distance from the input zone, for various temperatures and  $Re$  numbers of the film, is represented in Figs. 16...19.

The flow regime and the temperature of the heating agent have a significant influence on the values of the partial heat transfer coefficient in the thin film. At the same  $Re$  number and the same temperature of the heating fluid the partial heat transfer coefficient significantly increases with increasing  $Re$  number of the film.

The increase of solution concentration, which leads to the consistency increase, determines the diminution of the film transfer coefficient.

## 5. Conclusions

In the thin film flow of the polyethylene oxide solutions the partial heat transfer coefficient at the film side is strongly affected by the  $Re$  number and temperature of the heating fluid.

The main resistance to the heat transfer is located near the solid surface in a layer of about 10  $\mu\text{m}$  at all distances from the input zone, in the zone of smooth flow.

## Notations

- $d$  — diameter, [m];
- $g$  — gravity acceleration, [ $\text{m/s}^2$ ];
- $H$  — height of the surface the flow takes place on, [m];
- $k$  — index of consistency, [ $\text{kg/m sec}^{2-n}$ ];
- $K$  — overall heat transfer coefficient, [ $\text{W/m}^2 \text{ gr}$ ];
- $n$  — index of flow (flow index);
- $t_{1f}$  — inlet temperature of the film, [ $^{\circ}\text{C}$ ];
- $t_{2f}$  — outlet temperature of the film, [ $^{\circ}\text{C}$ ];
- $t_{1AC}$  — inlet temperature of the heating fluid, [ $^{\circ}\text{C}$ ];
- $t_{2AC}$  — outlet temperature of the heating fluid, [ $^{\circ}\text{C}$ ];
- $t_{mp}$  — wall average temperature, [ $^{\circ}\text{C}$ ];
- $t_{mf}$  — film average temperature, [ $^{\circ}\text{C}$ ];
- $Dt_1$  —  $t_{mp} - t_{mf}$  — temperature difference, [ $^{\circ}\text{C}$ ];
- $Dt_m$  — minimum temperature difference at the ends of the heat exchanger, [ $^{\circ}\text{C}$ ];
- $Dt_M$  — maximum temperature difference at the ends of the heat exchanger, [ $^{\circ}\text{C}$ ];
- $Dt_m \log$  — mean temperature difference;
- $w$  — rate of the heating fluid, [ $\text{m/s}$ ];

$$Re_{\text{int}} = \frac{Wd \rho_{AC}}{\eta_{AC}} - \text{Reynolds number for the heating fluid};$$

$$Re_F = \frac{\eta_{AC}}{12n} \cdot \frac{\Gamma}{2n+1} \left( \frac{\delta g \rho_F}{k} \right)^{1/n} - \text{Reynolds number of the film};$$

$$Ga_F = H^3 g \left( \frac{\rho_F}{k} \right)^{2/n} - \text{Galileu number of the film};$$

$$\alpha_F - \text{partial heat transfer coefficient at the film, } [\text{W/m}^2];$$



- $h_0$  — mean thickness of the film in the smooth zone, [mm];  
 $\eta_{AC}$  — viscosity of the heating fluid, [Pa.s];  
 $\rho_F$  — density of the fluid flowing in thin film, [Kg/m<sup>3</sup>];  
 $\rho_{AC}$  — density of the heating fluid, [Kg/m<sup>3</sup>];  
 $\Gamma$  — volume flow rate per unit width, [m<sup>2</sup>/s].

Received, June 19, 1986

Institute for Macromolecular Chemistry  
 „Petru Poni“, Jassy, Romania  
 and  
 Polytechnic Institute, Jassy,  
 Department of Chemical Engineering

## REFERENCES

1. Adams M.C., Drew T.B., Bays C.S., Trans. ASME, **62**, 627 (1940).
2. Davies E. I., Ind. Eng. Chem. Fund., **8**, 153 (1969).
3. Davies J. T., Shawki A.N., Chem. Eng. Sci., **29**, 1081—1088 (1974).
4. Ishigai S., Nakanisi S., Takehara M., Oyabu Z., Bul. of the ISME, **17**, 103, 106—114 (1974).
5. Leonard W. K., Estrin J., AIChE J., **18**, 2, 439—442 (1972).
6. Mukerje D., Davis E. J., AIChE J., **18**, 1, 94—101 (1972).
7. Nuselt W., Ver. Deut. Ing., **67**, 206 (1923).
8. Norman W. S., Mc. Intyre V., Trans. Inst. Chem. Eng., **38**, 301 (1960).
9. Ponter A. B., Alamir A. A., Mangers R. I., Tenside Detergents, **17**, 306—313 (1980).
10. Ponter A. B., Davies G. A., AIChE J., **12**, 1029 (1966).
11. Ponter A. B., Davies G. A., Chem. Eng. Sci., **23**, 6, 664 (1968).
12. Yih S. M., Liu J. L., AIChE J., **29**, 6, 903—909 (1983).
13. Wilke W., Ver. Deut. Ing. Forsch., 490 (1962).
14. Silvester N. D., Tyler J. S., Skelland A.U.P., The Canadian J. of Chem., Eng., **51** (1973).
15. Tudose R. Z., Naforniță C., Revue Roumaine de Chimie, **25**, 1, 155—163 (1980).
16. Vitan F., Studiul curgerii lichidelor în filme subțiri. Ph. D. Diss., Polyf. Inst., Jassy, 1985.

## STUDIUL EXPERIMENTAL AL TRANSFERULUI TERMIC LA CURGEREA ÎN FILME SUBȚIRI DE LICHIDE NENEWTONIENE

(Rezumat)

Se stabilește o corelație pentru coeficientul parțial de transfer termic la curgerea în filme subțiri a unor lichide nenewtoniene.

Cu creșterea numărului  $Re$  al filmului și al lichidului încălzitor crește coeficientul parțial de transfer termic de partea filmului, iar cu creșterea viscozității are loc o scădere a acestuia.

SELECTION AND DESIGN OF THE COMPRESSORS FOR  
AMMONIA INDUSTRY

BY

ILIE SIMINICEANU

## 1. Introduction

Nowadays the industrial output of ammonia amounts to roughly 100 million t/year and approximately 100 million of crude oil or its equivalent in other energy sources are consumed. This enormous energy consumption is the predominant area of concern in the nitrogen industry today [1]. The majority of large plants, exporting ammonia at  $-33^{\circ}\text{C}$ , based on hydrocarbon reforming, have a compression system that uses about  $8 \times 10^6$  J/kg  $\text{NH}_3$ , equal to 20% of the total energy for ammonia production. This compression system includes: compression of natural gas and air before reforming, synthesis gas compression, recycle gas compression plus compression of ammonia vapour to supply refrigeration in the synthesis loop, as shown in Fig. 1.

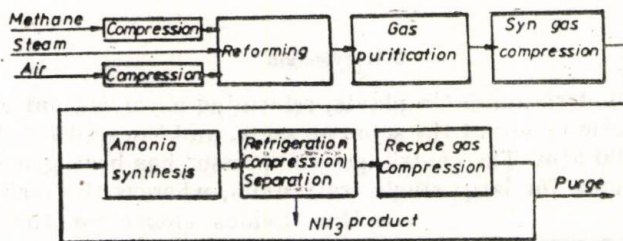


Fig. 1. — Simplified process flowsheet of an ammonia plant.

The syngas, makeup and recycle compressors account for 50 to 60% of the total compression power, depending on the synthesis loop pressure, the air and methane compressors account for 24%. The refrigeration compressor accounts for 20% [2].

Designers have reduced the compression energy requirement in some plants by substituting the mechanical refrigeration with the absorption one, which utilizes low level waste heat from the process or a flue gas stream. In a few ammonia plants, the condensing turbine drive for the air compressor has been replaced by a gas turbine drive. Further improvements of the compression systems for ammonia plants are however possible by a proper selection of the compressor types and their accurate design.

The criteria of selection of the compressor type and the basic equations for simplifying calculations, from a chemical engineer's point of view, are given in this paper.



## 2. Compressor Types and Selection

The principal types of compressor used in the chemical industry are : reciprocating, centrifugal, axial-flow and rotary compressors.

a) *The Reciprocating Compressors* are suitable for high pressure and low flow processes. They are generally considered for applications where the inlet gas rate is about 5,000 m<sup>3</sup>/h or less. The maximum discharge pressure ranges from more than 4,000 atm for small machines to about 200 atm for larger units. The maximum compression ratio per stage is usually about 3 to 4. The outlet temperature and the mechanical stress usually limit the compression ratio. The mechanical design limit is usually 175°...200°C but lower temperatures may be required, depending on the gas properties: corrosiveness, tendency to form polymer or gum, or undergo other chemical reactions, reactivity with the compressor lubricating oil, oxidation or explosion possibilities, etc.

b) *The Centrifugal, or Radial Turbo-Compressors* are used for process applications from about 850 to 340,000 m<sup>3</sup>/h. The performance of the centrifugal compressors can usually be approximated by the "fan laws". The volumetric flow rate varies approximately with rotating speed, the head with the square of speed and the power input with the cubic of speed. The maximum compression ratio per stage is limited by the outlet temperature. The usual limit is 260°...280°C because they have diaphragms between impellers which tend to expand radially, due to the temperature rise. Sometimes, the compression ratio is set by maximum number of impellers that manufacturer can provide within a single casing (up to about 6...8).

The operating range for a centrifugal running at fixed speed is typically from 100 % to about 50 % of the design flow. The low end of this range is set by the surge point, where operation becomes unstable due to flow oscillation and vibration.

c) *The Axial Turbo-Compressors* are generally used for clean, non-corrosive gases, since these machines are more susceptible to deposits corrosion and erosion than the centrifugals ones. They are suitable for high flow rates (125,000...1,000,000 m<sup>3</sup>/h), and low pressures (9...10 atm). The operating range for an axial, running at fixed speed is much narrower than that of the centrifugals since the surge point is usually 85...95 % of design capacity. The outlet temperature limit is about 315°C.

d) The common types of *Rotary Compressors* are : helical screw, spiral axial, straight lobe, sliding vane, liquid ring. Their maximum flow ranges from 10,000 m<sup>3</sup>/h (sliding vane) to 50,000 m<sup>3</sup>/h (straight lobe). The overall efficiencies range from 50 % (liquid ring) to 75 % (helical screw).

### 2.1. Selection

In the modern ammonia plants, reforming is carried out at 30...40 atm, all the purification steps at the same pressure, and the synthesis loop is carried out at 135...300 atm. The centrifugal compressor has been generally accepted as the best choice for large single train units, whereas the reciprocating type

was the obvious choice for the small plants. The main question is the capacity level at which the balance swings from one to other. For several years, the consensus was about 600 t NH<sub>3</sub>/day as the dividing point. It is difficult to generalize, however, because so many factors are involved, namely : flow rate, maximum pressure developed, reliability, turn-down, control, type of drive, investment and operating costs, type of operation.

Fig. 2 shows the approximate ranges of application for the main types of compressors taking into account only the first two factors : the discharge pressure and the inlet flow rate.

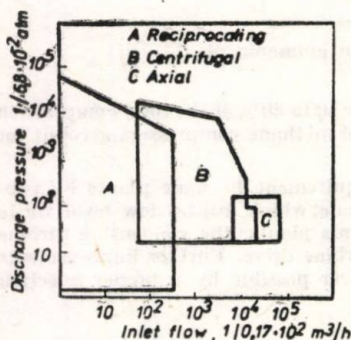


Fig. 2. — Approximate ranges of application for the main types of compressors [3].

### 3. Compressor Design

A given compressor can be analysed by using one of the following calculation models: isothermal, adiabatic and polytropic.

a) *The Isothermal Calculation Model* has the advantage of supplying the minimum theoretical power requirement, assuming the heat of compression is fully removed by cooling. The basic assumption is that the temperature of the compressed gas never increases above the inlet temperature. Generally, this is not achieved or even approached in a industrial-scale compressor.

The theoretical power,  $W_{is}$ , for a reversible isothermal compression is:

$$(1) \quad W_{is} = P_s V_s \ln \frac{P_d}{P_s},$$

where  $P_s$  and  $P_d$  are the gas pressures at suction and discharge, respectively. The heat of compression makes the gas temperature to rise, increasing the power requirement over the isothermal value computed by Eq. (1). The power delivered to the gas in a real compressor,  $W_g$ , and the brake power delivered by the driver,  $W_b$ , can be related to a reversible isothermal compressor by using, respectively, the following equations:

$$(2) \quad W_g = \frac{W_{is}}{\eta_{is}}, \quad (3) \quad W_b = \frac{W_{is}}{\eta_{is}\eta_m} = \frac{W_{is}}{\eta_{is0}},$$

where:  $\eta_{is}$  is the isothermal efficiency,  $\eta_m$  — the mechanical efficiency and  $\eta_{is0}$  — the overall isothermal efficiency.

b) *The Adiabatic Calculation Model* is widely used for reciprocating and rotary compressors. The theoretical power requirement,  $W_{ad}$ , is given by

$$(4) \quad W_{ad} = \frac{P_s V_s}{m} \left[ \left( \frac{P_d}{P_s} \right)^m - 1 \right],$$

where:  $m = (k-1)/k$  — adiabatic exponent;  $k = C_p/C_v$  — molar specific heat ratio. Although the Eq. (4) is established for an ideal gas with a constant specific heat, it gives fairly accurate results for real gases. It can be applied to real compressors using appropriate efficiency correlations:

$$(5) \quad \eta_{ad} = \frac{W_{ad}}{W_g}, \quad (6) \quad \eta_m = \frac{W_g}{W_b}.$$

The overall adiabatic efficiency ( $\eta_{ad0}$ ) will be

$$(7) \quad \eta_{ad0} = \frac{W_{ad}}{W_b} = \eta_m \eta_{ad}.$$

When the polytropic efficiency is known the adiabatic efficiency can be estimated by the equation:

$$(8) \quad \eta_{ad} = \frac{(P_d/P_s)^m - 1}{(P_d/P_s)^{m'} - 1}.$$



The discharge temperature for an adiabatic stage of compression ( $T_d$ ) is given by

$$(9) \quad T_d = T_s \left( \frac{P_d}{P_s} \right)^m.$$

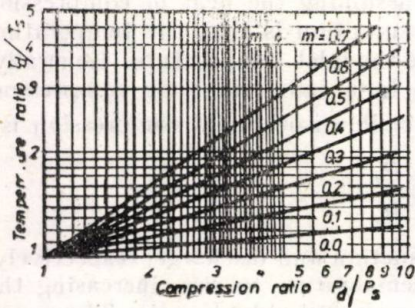


Fig. 3. — Temperature ratio  $T_d/T_s$  vs. compression ratio  $P_d/P_s$ .

This relation is plotted in Fig. 3.

c) *The Polytropic Compression Model* considers the compressor as a heat transfer device. This model is especially useful for radial and axial turbo-compressors. The polytropic compression follows the equation  $PV^n = \text{const}$ . The basic equation for one-stage of polytropic compression are analogous to those for an adiabatic one:

$$(10) \quad W_{\text{pol}} = \frac{P_s V_s}{m'} \left[ \left( \frac{P_d}{P_s} \right)^{m'} - 1 \right],$$

where:  $m' = (n-1)/n$  — polytropic exponent and  $n$  — exponent of the basic polytropic relation.

The polytropic exponent can be computed from the specific heat ratio ( $k$ ) and the polytropic efficiency :

$$(11) \quad m' = \frac{1}{\eta_{\text{pol}}} \left( \frac{k-1}{k} \right) = \frac{m}{\eta_{\text{pol}}}, \quad (12) \quad \eta_{\text{pol}} = \frac{(k-1)/k}{m'/(n-1)/n}.$$

The polytropic efficiency is usually estimated from the empirical correlations. The Fig. 4 gives approximate polytropic efficiencies for radial and axial turbo-compressors.

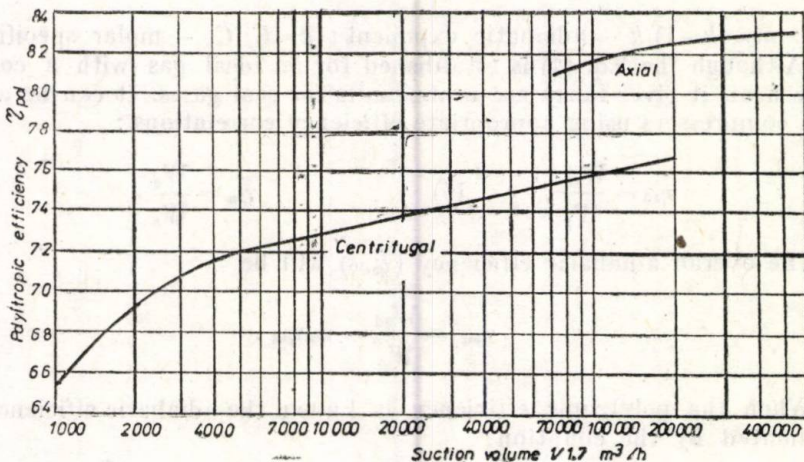


Fig. 4. — Approximate polytropic efficiency for radial and axial turbo-compressors [3].

The outlet temperature is computed by a relation analogous to the isentropic Eq. (9), plotted in Fig. 3.

In a multistage system, the polytropic formulas must be applied separately to each stage as in the adiabatic compression. A stage of compression may be defined as one or more units in series with no intercoolers between units. A radial or axial turbo-compressor casing with multiple impellers and no intermediate coolers is thus a single stage of compression.

Eq. (13) correlates the overall compression ratio of a multiple stage unit ( $z_0$ ) and the  $N$  stages of compression with the same compression ratio for each stage ( $z$ ):

$$(13) \quad N = \log \frac{z_0}{z}.$$

This equation neglects the pressure drop across the intercoolers, separators, interstage piping, etc. The number of stages is often set by the maximum discharge temperature limit. The outlet temperature in a multiple stage system should be computed by energy balance.

#### 4. Conclusions

A chemical engineer can select the types of compressor used in ammonia industry employing the equations and charts presented here above, but the complex design and construction of these machines is not possible without the decisive contribution of the mechanical engineer.

Received, February 11, 1985

Polytechnic Institute, Jassy,  
Department of Chemical  
Inorganic Technology

#### REFERENCES

1. Calistru C., Leonte C., Siminiceanu I., Hagiu C., *Technologia îngrășămintelor minerale*. Vol. I, Ed. Tehn., Buc., 1984.
2. Stokes K. J., *Chem. Eng. Process*, **7**, 88 (1979).
3. Dimoplan W., *Hydrocarbon Processing*, **5**, 221 (1978).

#### SELECTAREA ȘI PROIECTAREA COMPRESOARELOR PENTRU INDUSTRIA AMONIAICULUI

(Rezumat)

Procesele din industria amoniacului se desfășoară la presiuni ridicate. O fabrică contemporană de mare capacitate include un sistem de comprimare care consumă circa  $8.10^6$  J/kg  $\text{NH}_3$ , ceea ce reprezintă 20% din consumul total de energie al instalației de producere a amoniacului.

Se prezintă, din punctul de vedere al inginerului chimist, criteriile de selectare și o metodă de proiectare rapidă a compresoarelor pentru industria amoniacului.





## UREA-AMMONIUM PHOSPHATES FERTILISERS

BY

CAROLINA HAGIU

## 1. Introduction

The procedures of obtaining complex urea-ammonium phosphates fertilizers by combining the urea flowsheets with those of phosphoric acid can be accomplished in various technological variants, as a function of the peculiarities of technological procedures of urea obtaining. The analysis of the technological versions proposed by authors on the basis of mathematical models of mass and thermal balances [1] leads to the conclusion that using the urea solutions from stripping and first stage expansion, suspensions of urea-ammonium phosphates fertilizers with a  $N : P_2O_5$  ratio varying between 1:0.6 and 1:1.2, with a moisture content of 20...30% are obtained, which can be sent to granulation with or without previous concentration. In case of using the solutions resulted from the second stage of expansion, with a low  $NH_3$  content fertilizer suspensions, with  $N : P_2O_5 = 1 : 0.067$  are obtained, unsuitable for the common fertilizers; this variant implies the correction of  $N : P$  ratio by introducing in the technological sheet a new preneutralizing process of the phosphoric acid and by changing the  $m_{urea}^0 : m_{acid}^0$  ratio.

In these paper the experimental results concerning the investigation of the possibilities of converting the urea solutions of various compositions into urea-ammonium phosphates fertilizers, by using two technological versions with and without preneutralization of the phosphoric acid are reported. The influence of the composition of reagent phases, the phase ratio and duration of the process achievement on the quality of the obtained fertilizers is investigated.

## 2. Experimental Results and Discussion

Urea solutions and suspensions of various compositions have been used, as follows: solutions taken from stripping Stamicarbon equipments after expansion at 3.5 and 1 ata (the solutions 1 and 2), Stamicarbon with working the liquid phase by expansion in two stages (solution 3 — after expansion, the second stage) and the synthetic solution in the urea— $NH_4OH$ — $H_2O$  system (solution 4). The composition of urea solution is given in Table 1.



Table 1  
Composition of Urea Solution

| Solution | Composition, [%]           |                                    |                                     |               |                      |
|----------|----------------------------|------------------------------------|-------------------------------------|---------------|----------------------|
|          | $(\text{NH}_2)_2\text{CO}$ | $(\text{CO}_2)_{\text{carbamate}}$ | $\text{NH}_2-\text{CO}-\text{NH}_4$ | $\text{NH}_3$ | $\text{H}_2\text{O}$ |
| 1        | 61.2                       | 3.09                               | 5.47                                | 4.28          | 29.05                |
| 2        | 71.5                       | 0.21                               | 0.37                                | 0.58          | 27.55                |
| 3        | 64.91                      | 0.26                               | 0.47                                | 0.30          | 34.22                |
| 4        | 39.50                      | —                                  | —                                   | 5.89          | 44.61                |

The laboratory equipment consisted of a discontinuous reactor, with mechanical stirring, thermally insulated, provided with feed and outlet connections and test cock, control thermometer and gas removal connection. The process has been accomplished in an adiabatic thermal regime, the evolved heat determining the increase of the reaction mass temperature and water evaporation so that a fertilizer paste be finally obtained.

For accomplishing the variant with ammonia preneutralization a reactor for ammonia bubbling has also been included. The sketch of the experimental equipment is depicted in Fig. 1.

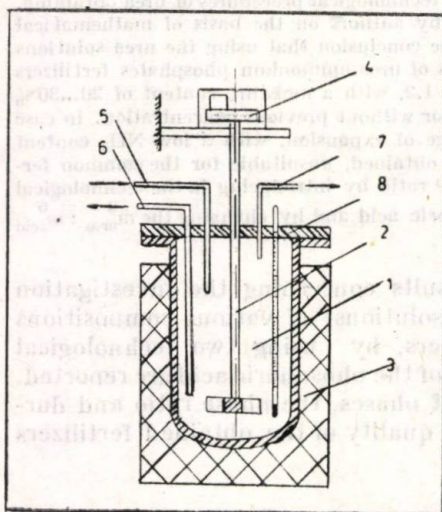


Fig. 1. — Diagram of the experimental equipment: 1 — Reactor; 2 — Stirrer; 3 — Thermal insulation; 4 — Motor-reduction gear; 5, 6 — Feed connection and sampling device; 7 — Gas removal connection; 8 — Control thermometer.

To settle the optimum conditions for obtaining various sorts of fertilizers the influence of the chemical composition of reagent phases, of the phase ratio and of the residence time on the quality of the obtained fertilizers has been investigated, according to two versions of the technological process: with and without acid preneutralization.

The quality of the urea-ammonium phosphates fertilizer has been determined by means of the  $\text{N}:\text{P}_2\text{O}_5$  ratio. For determination of the

$P_2O_5$  content, the gravimetric method of precipitating with quinoleine phosphate [2] has been used, the overall nitrogen being determined by Kjeldahl method [3].

### 2.1. Influence of the Residence Time

Using the synthetic solution 4, phosphoric acid with a content of  $x_{P_2O_5} = 0.3209$ , and carrying the process in thermal adiabatic regime for residence times varying between 5 and 30 min. the results listed in Table 2 have been obtained.

Table 2

*Influence of Residence Time*

| No. | Time<br>min. | Tem-<br>per-<br>ature<br>°C | Suspension composition,                       |                                   |                                      | Fertilizer type |
|-----|--------------|-----------------------------|-----------------------------------------------|-----------------------------------|--------------------------------------|-----------------|
|     |              |                             | $\bar{x}_{N_{\text{overall}}} \cdot 100$<br>% | $\bar{x}_{P_2O_5} \cdot 100$<br>% | $\frac{\bar{x}_N}{\bar{x}_{P_2O_5}}$ |                 |
| 1   | 5            | 58                          | 16.56                                         | 10.51                             | 1.57 : 1                             | 1 : 0.636       |
| 2   | 10           | 59                          | 16.73                                         | 10.54                             | 1.58 : 1                             | 1 : 0.633       |
| 3   | 20           | 58                          | 16.45                                         | 10.54                             | 1.56 : 1                             | 1 : 0.641       |
| 4   | 30           | 58                          | 16.64                                         | 10.53                             | 1.58 : 1                             | 1 : 0.633       |

The process is found to proceed at high rates, after five minutes the suspension composition remaining practically constant the heat of reaction determines the increase of reaction mass temperature up to 58°...59°C and water evaporation, fertilizer suspensions with N :  $P_2O_5$  ratio of 1.56...1.58 to 1 being obtained.

### 2.2. Influence of the Chemical Composition and of the Reagent Phase Ratio

The ratio of reagent phase is thus calculated as to assure the neutralization of free ammonia and of that found as carbamate in the urea solution up to an ammonization degree  $\eta_A = 1.5$  [4].

Based on the mass balance equations [1] and assuming that the decomposition of ammonia carbamate and  $CO_2$  desorption proceed completely, the following equation for calculating the phase ratio, has been derived:

$$(1) \quad \frac{m_{\text{urea}}^0}{m_{\text{acid}}^0} = \frac{0.434 \bar{x}_{H_2PO_4}^0}{\bar{x}_{NH_3, \text{free}}^0 + 0.434 \bar{x}_{\text{cm}}^0}$$

The influence of chemical composition of the solutions and of the mass ratio of the latter is pointed out in Table 3.

Using synthetic urea solutions of various compositions and phosphoric acid with  $x_{H_3PO_4}^0 = 0.685$  at a phase ratio comprised between 1.11 and 2.32, fertilizer suspensions with an overall active substance varying between 25.94%



**Table 3**  
Influence of the Chemical Composition and of the Reagent Phase Ratio

| No. | Urea solution                |                                   |                                 | Suspension composition       |                                   |                                      | Fertilizer type |
|-----|------------------------------|-----------------------------------|---------------------------------|------------------------------|-----------------------------------|--------------------------------------|-----------------|
|     | $\bar{x}_u^0 \cdot 100$<br>% | $\bar{x}_{NH_3}^0 \cdot 100$<br>% | $\frac{m_{urea}^0}{m_{acid}^0}$ | $\bar{x}_N^0 \cdot 100$<br>% | $\bar{x}_{P_2O_5} \cdot 100$<br>% | $\frac{\bar{x}_N}{\bar{x}_{P_2O_5}}$ |                 |
| 1   | 33.78                        | 8.12                              | 2.09 : 1                        | 14.55                        | 11.39                             | 1.27 : 1                             | 1 : 0.78        |
| 2   | 39.36                        | 8.94                              | 2.32 : 1                        | 17.68                        | 14.82                             | 1.19 : 1                             | 1 : 0.83        |
| 3   | 40.80                        | 15.40                             | 1.11 : 1                        | 14.84                        | 23.90                             | 0.62 : 1                             | 1 : 1.61        |

and 38.74% are obtained, the ratio between the essential nutrient element being comprised between (0.62...1.27) : 1.

### 2.3. Versions of Technological Process

The diversification of urea-phosphatic fertilizer sorts and the correction of N : P<sub>2</sub>O<sub>5</sub> ratio is possible by introducing in the technological sheet of a pre-neutralizing process of phosphoric acid. The experimental results obtained with urea solution taken from the industrial equipment with the composition given in Table 1 (solutions 1...3), using two variants of technological process, are listed in Tables 4 and 5.

**Table 4**  
Composition of the Suspension of Urea Ammonium Phosphates Fertilizers  
(Variant without Preneutralization)

| No. | Urea solution | $\bar{x}_{H_3PO_4}^0 \cdot 100$<br>% | $\frac{m_{urea}^0}{m_{acid}^0}$ | Suspension composition,    |                                   | Fertilizer type |
|-----|---------------|--------------------------------------|---------------------------------|----------------------------|-----------------------------------|-----------------|
|     |               |                                      |                                 | $\bar{x}_N \cdot 100$<br>% | $\bar{x}_{P_2O_5} \cdot 100$<br>% |                 |
| 1   | Solution 1    | 67.63                                | 3.9                             | 16.50                      | 10.22                             | 1 : 0.62        |
| 2   |               | 67.63                                | 4.0                             | 16.86                      | 9.97                              | 1 : 0.59        |
| 3   |               | 51.07                                | 2.9                             | 15.54                      | 9.51                              | 1 : 0.61        |
| 4   |               | 51.07                                | 3.3                             | 18.58                      | 8.80                              | 1 : 0.48        |
| 5   | Solution 2    | 67.63                                | 7.5                             | 19.38                      | 5.76                              | 1 : 0.29        |
| 6   |               | 67.63                                | 7.5                             | 19.82                      | 5.94                              | 1 : 0.29        |
| 7   |               | 51.07                                | 5.6                             | 18.63                      | 5.50                              | 1 : 0.29        |
| 8   |               | 51.07                                | 5.5                             | 18.10                      | 5.89                              | 1 : 0.32        |
| 9   | Solution 3    | 67.63                                | 54                              | 30.05                      | 0.88                              | 1 : 0.026       |
| 10  |               | 67.63                                | 55                              | 31.20                      | 0.83                              | 1 : 0.026       |
| 11  |               | 51.07                                | 44                              | 29.80                      | 0.82                              | 1 : 0.027       |
| 12  |               | 51.07                                | 45                              | 30.10                      | 0.818                             | 1 : 0.027       |

As can be seen in Table 4 the use of urea solutions with low ammonia content (free and in carbamate form) results in fertilizer suspensions with low P<sub>2</sub>O<sub>5</sub> content and respective N : P<sub>2</sub>O<sub>5</sub> ratio unusable in common fertilizers. The solutions from stripping (I) containing 4.28% free NH<sub>3</sub> and 5.47% carbamate lead to the obtaining of suspensions with N : P<sub>2</sub>O<sub>5</sub> = 1 : (0.48...0.62).

To correct the  $N : P_2O_5$  ratio a process of phosphoric acid preneutralization has been included in the process.

Table 5

Composition of the Suspensions of Urea-Ammonium Phosphates Fertilizers  
(Variant with Preneutralization)

| No. | Urea solution | $\frac{m_{urea}^0}{m_{acid}^0}$ | Suspension composition, [%] |                              | Fertilizer type |
|-----|---------------|---------------------------------|-----------------------------|------------------------------|-----------------|
|     |               |                                 | $\bar{x}_N \cdot 100$       | $\bar{x}_{P_2O_5} \cdot 100$ |                 |
| 1   | Solution 1    | 1                               | 16.38                       | 25.02                        | 1 : 1.50        |
| 2   |               | 1.66                            | 16.42                       | 18.65                        | 1 : 1.13        |
| 3   |               | 2                               | 16.75                       | 16.77                        | 1 : 1           |
| 4   | Solution 2    | 3                               | 17.15                       | 12.60                        | 1 : 0.73        |
| 5   |               | 1.5                             | 18.12                       | 20.50                        | 1 : 1.12        |
| 6   |               | 1.66                            | 18.55                       | 18.69                        | 1 : 1           |
| 7   |               | 2                               | 18.50                       | 16.46                        | 1 : 0.89        |
| 8   | Solution 3    | 3                               | 19.13                       | 12.45                        | 1 : 0.65        |
| 9   |               | 0.66                            | 21.53                       | 29.40                        | 1 : 1.36        |
| 10  |               | 1.00                            | 21.87                       | 23.84                        | 1 : 1.09        |
| 11  |               | 1.33                            | 22.94                       | 20.56                        | 1 : 1.89        |
| 12  |               | 1.66                            | 23.68                       | 17.76                        | 1 : 0.75        |

The experimental results obtained in the case of variant with acid preneutralization (Table 5) indicated that the suspensions have  $N : P_2O_5 = 1 : (0.65...1.5)$  which corresponds to the common fertilizers.

By changing the parameters of the technological process a large variety of urea-ammonium phosphates fertilizers of different compositions specific to various soils and cultures can be obtained.

### 3. Conclusions

The process of neutralization of the ammonia contained in the various urea solutions proceeds at a high rate with the removal of a significant water amount which leads to the obtaining of fertilizer suspensions which can be submitted to granulation with or without recirculation of the solid material.

The urea solutions with low ammonia content, resulting from the industrial equipment after expansion, lead to the obtaining of fertilizers with low  $P_2O_5$  content, unsuitable for common fertilizers. The correction of the  $N : P_2O_5$  ratio is accomplished by preneutralization of the acid with gases containing ammonia, coming also from the urea equipments.

The change of composition of urea solutions, of phase ratio and the introduction of a preneutralization process allow the obtaining of a wide game of urea-ammonium phosphates fertilizers.

Received, July 9, 1987

Polytechnic Institute, Jassy,  
Department of Chemical  
Inorganic Technology



## REFERENCES

1. Hagi C., Calistru C., IIIrd Symp. on Chemical Process Eng., P. Neamț, 345 (1983).
2. \* \* \* STAS 8623/3 (1970).
3. Liteanu C., Hopârțan E., *Chimie analitică cantitativă. Volumetrie*. EDP, București, 1972.
4. Hagi C., *Cercetarea procesului de amonizare a soluțiilor de acid fosforic* Ph. D. Diss., Polyt. Inst., Jassy, 1980.

## ÎNGRĂȘĂMINTE UREO-FOSFATICE

(Rezumat)

Se expun rezultatele cercetărilor experimentale privind obținerea îngrășămintelor ureo-fosfatice prin integrarea liniilor de uree, acid fosforic și / sau ortofosfați de amoniu. Modificarea parametrilor de realizare a procesului permite obținerea unei game variate de sortimente de îngrășăminte ureo-fosfatice, necesare diferitelor tipuri de soluri și culturi.

## KINETICS OF KCl DISSOLVING IN AMMONIUM FULPHATE SOLUTION

BY

STELIAN PETRESCU, C. CALISTRU and AL. SZÉP

## 1. Introduction

The study of the dissolving kinetics processes of a salt in an aqueous solution of another salt which contains different ionic species is less found in literature [1]...[3]. Literature presents many works dealing with the kinetics of dissolving of inorganic salts in water or in their aqueous solutions [4]...[10].

In the above quoted works [1]...[3] there is presented the macrokinetics and mathematical modelling of the dissolving process of KCl in ammonium sulphate solution based on the grain pattern.

Using the disk pattern, in what follows there is established a mathematical model which allows the determination of the dissolving rate and, respectively, of the mass transfer individual coefficient during solids dissolving.

The rate of potassium chloride dissolving in ammonium sulphate aqueous solution and the mass transfer individual coefficient are experimentally determined by using the disk pattern; on this basis the influence of kinetic parameters over the rate of global dissolving process is studied.

## 2. Determination of the Mathematical Pattern

With the aim to determine the mathematical pattern of the dissolving of a disk form grain in an aqueous solution there was begun from the definition relation of component A dissolving rate [11]:

$$(1) \quad V_D = - \frac{dn_A}{S d\tau},$$

where:  $n_A$  is the number of solute moles of disk grain at one time;  $S$  — the disk surface in contact with solution;  $\tau$  — the duration of the process.

The variation of the number of moles of component A in an infinitesimal period of time is:

$$(2) \quad dn_A = \frac{dm_A}{M_A} = \rho \frac{\bar{x}_A}{M_A} dV_{IIs} = \rho^* dV_{IIs}.$$



According to Fig. 1, the correspondent variation of the grain volume is :

$$(3) \quad dV_{(1)s} = \pi R^2 dh$$

and consequently :

$$(4) \quad dn_A = \pi R^2 \rho^* dh.$$

The disk surface in contact with liquid phase is unchanged in time and it is given by the relation :

$$(5) \quad S = \pi R^2.$$

Replacing relations [(4) and (5) in Eq. (1) it results the following equation for dissolving rate :

$$(6) \quad V_D = -\rho^* \frac{dh}{d\tau}.$$

Fig. 1. — Disk grain pattern.

As known, the degree of solute transformation is defined by the relation [11] :

$$(7) \quad \eta_A = \frac{n_A^0 - n_A}{n_A^0},$$

where :  $n_A^0$  is the number of solute moles from the initial grain ;  $n_A$  — the number of solute moles out of the grain at one time.

If the number of  $A$  moles is expressed by mass and there is passing to volume, is results :

$$(8) \quad \eta_A = 1 - \frac{m_{(1)s}}{m_{(1)s}^0} = 1 - \frac{h}{H}.$$

The height of disk at one time is given by the following relation :

$$(9) \quad h = H(1 - \eta_A).$$

Replacing relation (9) in (6) and taking into account that :

$$n_A^0 = \pi R^2 \rho^* H,$$

another form of the mathematical pattern of the solids dissolving occurs :

$$(10) \quad V_D = \frac{n_A^0}{\pi R^2} \cdot \frac{d\eta_A}{d\tau}.$$

In conditions when the elementary transfer process have a leading part in the dissolving rate, there is possible to write :

$$(11) \quad V_D = K_l(C_A^s - C_A).$$

Since the infinitesimal variation of solute moles number leads to an infinitesimal variation of the solution concentration, it results :

$$(12) \quad -dC_A = \frac{\pi R^2 \rho^*}{V_{\text{li}}^0} dh.$$

By integrations of Eq. (12) between the limits  $h=H$ ,  $C_A=0$  and  $h=h$ ,  $C_A=C_A$  we obtain :

$$(13) \quad C_A = \frac{\pi R^2 \rho^*}{V_{\text{li}}^0} (H-h).$$

Inserting relation (13) in Eq. (11) and using the following notation :

$$a = \left( \frac{C_A^e V_{\text{li}}^0}{\pi R^2 \rho^*} - H \right)^{-1}$$

it results :

$$(14) \quad V_D = K_l \left( C_A^e - \frac{\pi R^2 \rho^* H}{V_{\text{li}}^0} \right) (1+ah),$$

whence :

$$(15) \quad K_l = \frac{\rho^*}{(\pi R^2 \rho^* H / V_{\text{li}}^0 - C_A^e) (1+ah)} \cdot \frac{dh}{d\tau}.$$

Replacing Eq. (9) in (14) and (15),  $V_D$  and  $K_l$  become :

$$(16) \quad V_D = \frac{n_A^0 K_l}{V_{\text{li}}^0} [1 + a_1(1 - \eta_A)], \quad (17) \quad K_l = \frac{V_{\text{li}}^0}{\pi R^2 [1 + a_1(1 - \eta_A)]} \cdot \frac{d\eta_A}{d\tau},$$

where :

$$a_1 = \left( \frac{C_A^e V_{\text{li}}^0}{n_A^0} - 1 \right)^{-1}.$$

Eqs. (14)...(17) represent different forms of the mathematical pattern of solids dissolving in case when the elementary transfer process of potassium chloride through liquid phase is rate determinant.

In case when solute concentration in liquid phase is very small, ( $C_A \approx 0$ ), it may be neglected and the equations for the mass transfer individual coefficient become :

$$(18) \quad K_l = - \frac{\rho^*}{C_A^e} \cdot \frac{dh}{d\tau}, \quad (19) \quad K_l = - \frac{n_A^0}{\pi R^2 C_A^e} \cdot \frac{d\eta_A}{d\tau}.$$

### 3. Experimental Technique

Experimental determinations were made using a laboratory installation depicted in Fig. 2. The installation consists of a laboratory thermostat (1), a stirring flask (2) supplied with an agitator with blades (3).

In the flask there is immersed a support cylinder (4) (20 mm depth from the blade and 10 mm distance from the flask wall), with a potassium chloride disk inside (5). To check the temperature of the mass of the reaction the reactor is equipped with a contact thermometer (6).



The installation is supplied with a belt-drive system (7) connected to an electric engine (8), which is fixed to a support.

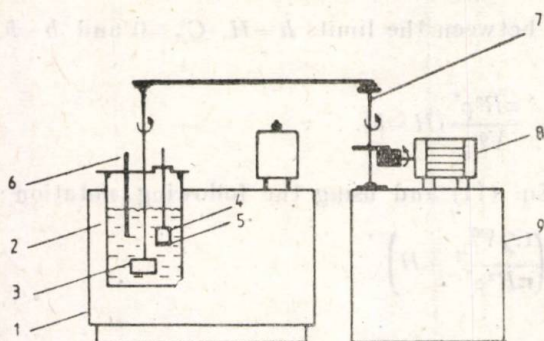


Fig 2. — Experimental installation.

Experimentally has been worked using chemically pure potassium chloride and an ammonium sulphate solution prepared from technical ammonium sulphate resulted by caprolactam synthesis. The potassium chloride disk was made by moulding grains with granulosity  $d_p < 0.045$  mm in the seat of the support cylinder.

For every kinetic curve, in reactor were introduced 500 ml of ammonium sulphate

solution of a certain concentration, the stirrer being switched on afterwards.

Reaching the prescribed value of temperature, in the stirring flask there were immersed successively six support cylinders with potassium chloride disks, which were beforehand weighed with an analytical balance. For every cylinder it was measured the contact time of the disk with ammonium sulphate solution. The contact time disk — solution was established as function of temperature, number of rotations and initial concentration of the ammonium sulphate solution.

At the end of the contact period of every cylinder, they were pulled out of reactor and put into an ethanol bath in order to remove the solution traces from the surface of the disk.

This operation take place in a very short time (approx. 10 sec.). The cleaning of the disk was followed by drying at  $100^\circ \dots 105^\circ$  C in a drying chamber. The dried disks together with the cylindrical support were weighed again.

By difference there was found the mass of potassium chloride passed into solution, respectively the amount of dissolved potassium chloride.

The variable parameters during the experiments were: temperature of the solution ( $T = 25^\circ; 40^\circ; 60^\circ$  C), initial concentration of ammonium sulphate solution ( $\bar{X}_{(\text{NH}_4)_2\text{SO}_4}^0 = 0,25; 0,35$ ), number of rotations of the stirrer ( $n = 230; 540$  r.p.m.).

#### 4. Results and Discussions

The obtained experimental data were used for the tracing of the kinetic curves  $\eta_{\text{KCl}}$  vs.  $\tau$ . In order to calculate the degree of potassium chloride transformation there was used the relation:

$$(20) \quad \eta_{\text{KCl}} = \frac{\sum_{i=1}^{n-1} m_i}{\sum_{i=1}^n m_i}$$



where:  $m_i$  is the potassium chloride dissolved of the disk;  $n$  — the total number of disks used for a single kinetic curve;

The  $\eta_{KCl}$  vs.  $\tau$  diagrams are represented in Figs. 3 and 4. The correlations found in these diagrams show that, for small amounts of dissolved potassium chloride, the transformation degree of KCl varies linearly during dissolution time. This observation point out that the dissolution rate of potassium chloride in ammonium sulphate solution is constant in time, in experiment conditions specified before.

Having in view the correlations from Figs. 3 and 4 were calculated the dissolution rate and the mass transfer individual coefficient of potassium chloride in ammonium sulphate solution.

Since the amount of dissolving KCl is small,  $C_{KCl} \approx 0$ , and to calculate the dissolving rate and the coefficient  $K_i$  were used Eqs. (10) and (19).

The mass transfer individual coefficient was calculated for the temperature of 25°C because, for the system  $K^+$ ,  $NH_4^+ / Cl^-$ ,  $SO_4^{2-}$ ,  $H_2O$  exist equilibrium data only for this temperature.

The obtained results are shown in Fig. 5 and in Table 1.

Table 1

*Variation of Dissolving Rate  $V_D$  and  $K_i$  Coefficient with Concentration and Number of Stirrer Rotations*

|                                              | n<br>r.p.m. | $C^0$ , [mass %] |        |
|----------------------------------------------|-------------|------------------|--------|
|                                              |             | 25               | 35     |
| $10^5 \times V_D$<br>Kmol/m <sup>2</sup> . s | 230         | 3.0855           | 2.2978 |
|                                              | 540         | —                | 3.2225 |
| $10^5 \times K_i$<br>m/s                     | 230         | 2.3767           | 2.1152 |
|                                              | 540         | —                | 2.9667 |

From Fig. 5 it may be observed that the dissolving rate of KCl in ammonium sulphate solution increases with the growth of temperature.

Further on, using experimental data there was determined the apparent activating energy of dissolving process, applying with that end in view the graphic method.

Representing the dependence  $\lg 1/\tau$  vs.  $-1/T$  (Fig. 6), according to Arrhenius equation, the activation energy is given by the slope of the resulting straight lines. The diagram from Fig. 6 indicates, for dissolving KCl in ammonium sulphate solution of 35% mass concentration, the apparent activation energy of 6 398 cal/mol, in the temperature range 25...60°C, for any values of transformation degree of potassium chloride. In connection with facts below there is obviously that in temperature range 25...60°C, the elementary transfer process of KCl is rate determinant.

As shown in Table 1, the dissolving rate of potassium chloride in ammonium sulphate solution is increased by the number of rotations and decreased by the concentration of ammonium sulphate initial solution.



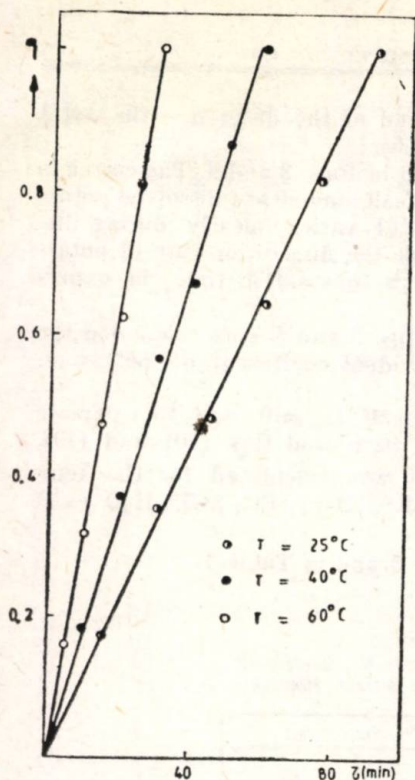


Fig. 3. — Dependence  $\eta_{KCl}$  vs.  $\tau$ ;  $n = 230$  r.p.m.,  $\bar{x}_{(NH_4)_2SO_4}^0 = 0.35$ .

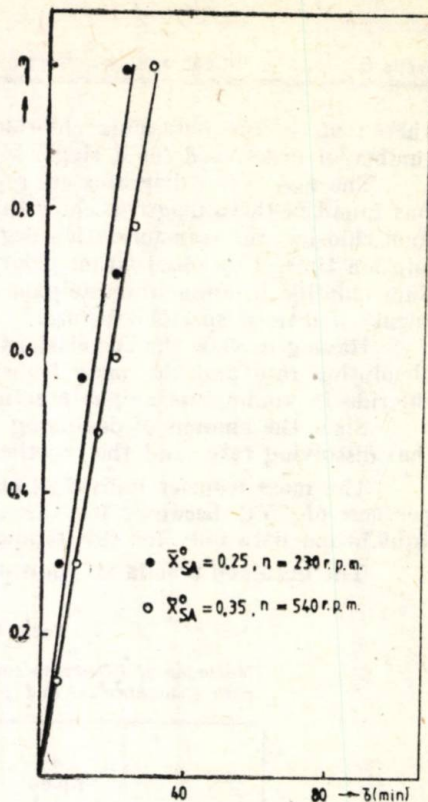


Fig. 4. — Dependence  $\eta_{KCl}$  vs.  $\tau$ ;  $T = 25^\circ C$ .

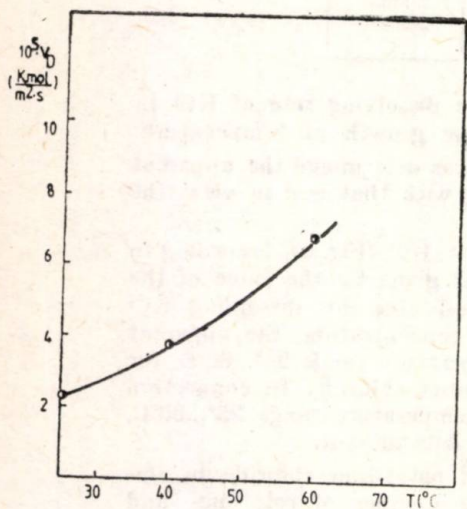


Fig. 5. — Dependence  $V_D$  vs.  $T$ ;  $n = 230$  r.p.m.,  $\bar{x}_{(NH_4)_2SO_4}^0 = 0.35$ .

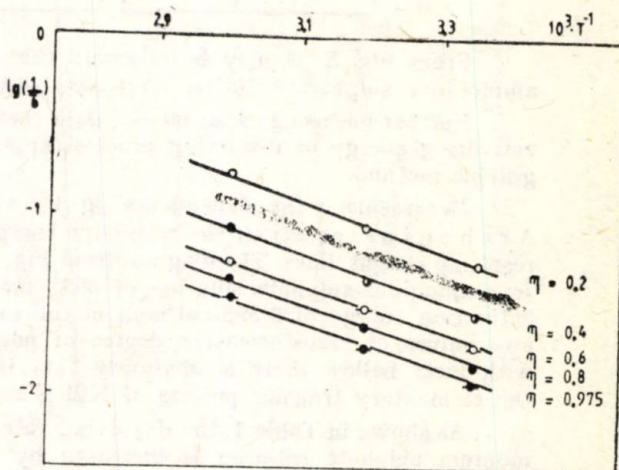


Fig. 6. — Dependence  $\lg 1/\tau$  vs.  $1/T$ ;  $n = 230$  r.p.m.,  $\bar{x}_{(NH_4)_2SO_4}^0 = 0.35$ .

At regards the mass transfer individual coefficient it increases with the number of rotations and decreases with growing concentration of ammonium sulphate initial solution.

These data point out too the fact that at low temperatures, the elementary transfer process of potassium chloride through liquid phase is speed determinant of the global process.

## 5. Conclusions

It was established a mathematical pattern for dissolving the disk form grains which allows experimental determination of the dissolving rate and of the mass transfer individual coefficient.

Using this pattern, the experimental values of the dissolution rate and of the mass transfer individual coefficient were determined by potassium chloride disk — form grains dissolving in an aqueous solution of ammonium sulphate at different concentrations, temperatures and number of rotations of the stirrer.

There was studied the influence of kinetic parameters upon the global dissolving process rate and established the rate determinant elementary process in certain experimental conditions.

## Notations

- $C_A^e$  — equilibrium solute concentration, [Kmol/m<sup>3</sup>];  
 $C_A$  — solute concentration at one time, [Kmol/m<sup>3</sup>];  
 $\rho^*$  — molar density of the solute, [Kmol/m<sup>3</sup>];  
 $H$  — initial height of the disk, [m];  
 $h$  — height of the disk at one time, [m];  
 $R$  — radius of the disk, [m];  
 $l, s$  — liquid, solide;  
[ ] — phase.

Received, February 25, 1988

Polytechnic Institute, Jassy,  
Department of Analytical and  
Inorganic Chemistry and  
Chemical Inorganic Technology

## REFERENCES

1. Calistru C., Leonte C., Petrescu St., The Third Symp. on Chemical Processes Engineering, P. Neamț, 1983, 57.
2. Calistru C., Petrescu St., Tordai E., Bul. șt. stud., Inst. polit. Iași, **IX**, 30 (1984).
3. Petrescu St., *Cercetarea de inginerie chimică a procesului de obținere a sulfatului de polasiu prin valorificarea soluției de sulfat de amoniu rezultată la fabricarea caprolactamei*. Ph. D. Diss., Polyt. Inst., Jassy, 1987.
4. Ruckenstein E., St. cerc. chim., **15**, 1, 1 (1967).
5. Sherwood T. R., Pigford R. L., Wilke C. R., *Mass Transfer*. McGraw-Hill, New York, 1975.
6. Mullin J. W., Nienow A. W., J. Chem. Eng., **9**, 4, 526 (1964).
7. Bovington C. H., Jones A. L., Trans. Farad. Soc., **55**, 8, 2088 (1970).
8. Boon Long S., Laguerie C., Coudere J. P., Chem. Eng. Sci., **33**, 7, 813 (1978).



9. Inoue A., Tsujino T., Ind. Eng. Chem. Process Des. Dev., **23**, 1, 122 (1984).
10. Trambouze P., Van Landeghem H., Wauquier J. P., *Les réacteurs chimiques*. Ed. Technip, Paris, 1984.
11. Calistru C., Leonte C., *Tehnologia substanțelor anorganice*. EDP, București, 1972.

## CINETICA DIZOLVĂRII KCl ÎN SOLUȚIE DE SULFAT DE AMONIU

(Rezumat)

Se stabilește un model matematic al dizolvării solidelor pe baza căruia se poate calcula viteza de dizolvare și coeficientul individual de transfer de masă.

Rezultatele obținute pun în evidență influența parametrilor cinetici asupra vitezei procesului de dizolvare a clorurii de potasiu sub formă de discuri, în soluție apoasă de sulfat de amoniu, precum și procesul elementar, determinant, de viteză.

## DÉTERMINATION DE QUELQUES CARACTÉRISTIQUES DU TALLOÏL BRUT

PAR

SAVEL IFRIM, CRISTINA LUCHIAN et MILITINA BOURCEANU

### 1. Introduction

Le talloïl brut est un mélange homogène de substances organiques ayant une grande valeur par ses multiples possibilités d'utilisation. Pratiquement c'est un sous-produit de la fabrication de la cellulose par le procédé „sulfate“.

On connaît que dans la composition du talloïl il y a un grand nombre de produits chimiques, appartenant surtout aux catégories des acides résiniques, des acides gras saturés et non-saturés, des produits insaponifiables, tels que des alcools, des stérols et des hydrocarbures [1]. Il peut également contenir un très petit pourcentage de substances volatiles, ainsi que traces d'eau (environ 2% ou plus).

La composition chimique du talloïl varie en larges limites et elle dépend de plusieurs facteurs à savoir : l'espèce ligneuse utilisée dans le processus d'ébullition, la qualité du bois, la région géographique de croissance du celui-ci, l'âge du bois, etc.

À partir du talloïl, par usinage [2], [3], on peut séparer des acides gras, des acides résiniques, du colophane et également d'autres produits organiques importants, qu'on peut utiliser, à leur tour, dans l'industrie des savons, des laques et des vernis, des résines synthétiques et des onguents, à l'encollage du papier. On peut utiliser ainsi le talloïl dans le processus de flottation ou bien dans des buts analytiques [4]...[6].

Compte tenu de l'importance particulière de ce produit organique, dans le présent travail on détermine quelques caractéristiques plus importantes du talloïl brut, séparé au Combinat de Fibres, Cellulose et Papier, Dej.

### 2. Partie expérimentale

Le talloïl utilisé pour analyse se présente comme un liquide homogène, consistant et huileux, ayant une couleur brune et une odeur moins agréable, proche à celle des conifères. Le produit a une viscosité relative grande à la température ambiante, pourtant il coule d'une façon continue sous l'influence de la gravitation. Par chauffage vers 80°...100°C sa viscosité diminue et il devient plus fluide. Le talloïl est légèrement soluble en White-spirit, en méthanol et partiellement soluble en éthanol.

En solution diluée d'hydroxyde de sodium (10%) et également de carbonate de sodium concentrée, par chauffage, il se saponifie ; par dilution à l'eau et agitation mécanique on obtient des dispersions colloïdales ou même des solutions. En solution concentrée d'hydroxyde de sodium il se solidifie.



Pour caractériser le talloïl brut on a effectué les suivantes déterminations : l'humidité, l'indice d'acidité, le contenu des acides résiniques et des acides gras, l'indice de saponification, le contenu des substances insaponifiables et le pourcentage de cendre.

Afin de constater si ces caractéristiques changent dans un certain laps de temps, on a soumis à l'analyse des échantillons de talloïl séparés en 1981, 1983 et 1985.

Pour déterminer l'humidité et le pourcentage de cendre on a utilisé les méthodes classiques, connues.

La détermination de l'indice d'acidité est fondé sur le titrage d'une quantité de produit dissous en méthanol, avec une solution d'hydroxyde de potassium 0,5 n (en méthanol), en présence de bleu de bromothymol ; l'apparition de la couleur bleu indique l'équivalence. On utilise la relation :

$$\text{indice d'acidité} = \frac{56,1}{B} \frac{AN}{}, [\text{mg KOH/g produit}],$$

où :  $A$  — la solution de KOH, ayant le titre connu, [ml],  $N$  — la normalité de la solution alcaline,  $B$  — le poids de l'échantillon, [g].

Le dosage des *acides résiniques* a été effectué comme suit : dans un ballon de 250 ml on pèse par voie analytique le produit à analyser, on introduit 100 ml méthanol et 50 ml solution d'acide sulfurique en méthanol (400 ml méthanol et 5,43 ml acide sulfurique concentré,  $d=1,831$ ). On reflue au bain-marie 30 min. Après refroidissement on y ajoute 1 ml de bromothymol (0,1 g pour 100 ml éthanol) et on titre avec une solution d'hydroxyde de potassium 0,5 n en méthanol, jusqu'à l'apparition d'une teinte marron-jaunâtre. En même temps on a suivi la valeur du pH, qui doit être égale à 4. On note avec  $a$  le nombre de ml de solution méthanolique de KOH utilisée. On continue le titrage jusqu'au virage de la solution vers vert-bleuâtre, en suivant toujours le pH, qui doit croître à 10,5. On note avec  $b$ , [ml], le volume de solution de KOH utilisée. Le contenu des acides résiniques est donné par la relation:

$$\% \text{ acides résiniques} = 30,2 \frac{AN}{B},$$

où :  $A = b - a$  — la solution méthanolique de KOH, [ml] ;  $N$  — la normalité de la solution de KOH ;  $B$  — le poids de l'échantillon, [g].

Le contenu en acides gras résulte par la différence :  $\% \text{ acides gras} = 100 - (\text{acides résiniques} + \text{substances insaponifiables})$ .

Pour déterminer l'indice de saponification on pèse l'échantillon dans un ballon de 250 ml et on ajoute 50 ml solution méthanolique de KOH 0,5 n. On reflue au bain-marie 30 min. On refroidit le ballon et sans laver le réfrigérant on titre la solution avec  $\text{H}_2\text{SO}_4$  0,5 n. Parallèlement on réalise une épreuve de contrôle, en titrant 50 ml de solution KOH 0,5 n avec la solution  $\text{H}_2\text{SO}_4$  0,5 n. L'indice de saponification est donné par la relation :

$$\text{I.S.} = \frac{56,1 (B - A) N}{C},$$



où :  $A$  — la solution de  $H_2SO_4$  0,5 n utilisée pour le titrage, [ml];  $B$  — la solution de  $H_2SO_4$  0,5 n utilisée pour le titrage de l'épreuve de contrôle, [ml];  $C$  — le poids de l'épreuve, [g];  $N$  — la normalité de la solution de  $H_2SO_4$ .

On réalise le dosage des *substances insaponifiables* de la manière suivante : dans un ballon à fond plat on pèse 5 g de talloïl, on y ajoute 15 ml solution alcoolique de KOH (132 g KOH en 150 ml de l'eau distillée et de l'éthanol jusqu'à 1 000 ml). On reflue 90 min. On ajoute 50 ml de l'eau distillée et on passe le contenu du ballon dans un entonnoir de séparation. On lave le ballon avec 40 ml éther, qui est introduit aussi dans l'entonnoir de séparation. On agite l'entonnoir et après la séparation des deux couches on passe la couche aqueuse dans un autre entonnoir de séparation. On effectue quatre extractions successives de 40 ml éther chacune, de la couche aqueuse.

On passe les extraits étheriques ensemble dans un ballon préalablement pesé. On distille l'éther et on sèche le résidu pendant 10...15 min. à 100...105°C, en étuve. Après refroidissement on pèse le ballon, on dissout le contenu en 50 ml isopropanol neutre et on titre avec une solution alcoolique d'hydroxyde de potassium 0,1 n, en présence du bleu de bromothymol. Pour calculer le contenu en substances insaponifiables on utilise la relation :

$$S.I. = \frac{A - 0,302 CN 100}{B}$$

où :  $A$  — le poids du résidu séché, [g];  $B$  — le poids de l'épreuve utilisée, [g];  $C$  — la solution de KOH 0,1 n utilisée au titrage, [ml];  $N$  — la normalité de la solution alcaline.

Tous les résultats des analyses sont présentés dans le Tableau 1.

Tableau 1

| Humidité<br>%            | Indice<br>d'acidité<br>mg KOH/g | Acides<br>résiniques<br>% | Acides<br>gras<br>% | Indice de<br>saponification | Substances<br>insaponifiables<br>% | Cendre<br>% |
|--------------------------|---------------------------------|---------------------------|---------------------|-----------------------------|------------------------------------|-------------|
| <i>Talloïl brut 1981</i> |                                 |                           |                     |                             |                                    |             |
| 1,0                      | 112,21                          | 70,60                     | 12,80               | 98,11                       | 20,65                              | 2,10        |
| 1,2                      | 111,80                          | 68,60                     | 14,20               | 99,26                       | 20,81                              | 2,90        |
| 1,4                      | 109,70                          | 66,50                     | 16,20               | 100,30                      | 18,66                              | 3,00        |
| Moyenne :<br>1,2         | 111,27                          | 68,56                     | 14,40               | 99,22                       | 20,04                              | 2,66        |
| <i>Talloïl brut 1983</i> |                                 |                           |                     |                             |                                    |             |
| 2,95                     | 83,08                           | 61,45                     | 20,26               | 109,39                      | 18,30                              | 5,02        |
| 3,04                     | 82,46                           | 61,62                     | 20,12               | 104,19                      | 18,78                              | 5,09        |
| 2,86                     | 84,06                           | 62,12                     | 21,00               | 103,00                      | 16,22                              | 4,66        |
| Moyenne :<br>2,95        | 83,20                           | 61,73                     | 20,46               | 105,33                      | 17,76                              | 4,92        |
| <i>Talloïl brut 1985</i> |                                 |                           |                     |                             |                                    |             |
| 2,99                     | 112,83                          | 66,61                     | 14,91               | 111,02                      | 18,48                              | 4,08        |
| 2,50                     | 109,49                          | 66,68                     | 15,10               | 110,96                      | 18,22                              | 4,20        |
| 2,40                     | 112,22                          | 66,83                     | 14,64               | 110,04                      | 18,53                              | 4,21        |
| Moyenne :<br>2,63        | 111,51                          | 66,71                     | 14,88               | 110,67                      | 18,41                              | 4,16        |



### 3. Interprétation des résultats

Par l'analyse des résultats enregistrés dans le Tableau 1 on observe qu'il n'y a pas de grandes différences concernant les caractéristiques du talloil brut. Pourtant on peut mentionner une diminution de l'indice d'acidité pour l'épreuve de 1983 et une augmentation du pourcentage en acides gras. On observe également, pour l'épreuve de 1981, un indice de saponification moindre que pour les deux dernières, résultat qui peut être expliqué par l'existence d'un pourcentage plus élevé en substances insaponifiables.

Les caractéristiques physiques du talloil, ainsi que le contenu réduit d'eau et de cendre, prouvent que ce produit est assez bien séparé au combinat de Dej, ayant une bonne pureté.

Dans tous les cas le contenu des acides résiniques est assez élevé et les données analytiques présentent une petite dispersion. Le pourcentage élevé des acides résiniques constitue un argument pour utiliser le talloil comme matière première pour la séparation de la colophane ou comme agent de l'encollage du papier, compte tenu que les acides résiniques sont les composants fondamentaux de la colophane, agent classique de l'encollage.

La présence d'une proportion importante d'acides gras recommande le talloil comme matière première pour obtenir ces produits, nécessaires pour la production des savons, des détergents, des laques, des teintures, etc. Même le talloil brut, sans autres usinages, peut servir à l'obtention des savons. Les acides carboxyliques favorisent l'utilisation du talloil pour obtenir des esters; ce sont les esters de tall utilisés à la préparation des laques.

Puisque le talloil contient des substances insaponifiables on peut l'utiliser pour isoler de tels produits parmi lesquels les plus connus sont les produits stéroliques.

Les observations présentées ci-dessus prouvent que le talloil séparé au combinat de Dej est un produit de grande valeur, en représentant une source de substances organiques et sa récupération s'avère nécessaire dans toutes les fabriques de cellulose où ça c'est possible.

### 4. Conclusions

On détermine les principales caractéristiques physico-chimiques du talloil brut, séparé au combinat de fibres, cellulose et papier — Dej. Ces caractéristiques sont déterminées pour le talloil séparé en différentes périodes, en résultant qu'il n'y a pas de différences importantes entre elles. Compte tenu de sa composition chimique, on indique les principales directions de mise en valeur de ce mélange de produits organiques. On recommande d'isoler le talloil dans toutes les fabriques de spécialité.

Reçue le 17 décembre 1986

Institut Polytechnique, Jassy,  
Chaire de Chimie générale  
et Technologie

## B I B L I O G R A P H I E

1. Lorens C., Peintures — Pigments — Vernis, **47**, 7, 388 (1971).
2. Трофимов А. Н., Бочарников Е. В., Узлов Г. А., Тобурда-  
новская Л. А., Коган В. Б., Гидрол. и лесохим. пром., **7**, 10 (1974).
3. Узлов Г. А., Жукова И. П., Гидрол. и лесохим. пром., **2**, 12 (1973).
4. Ciobanu D., Cecal Al., Rev. de chimie, **35**, 1, 68 (1984).
5. Ciobanu D., Cecal Al., Rev. de chimie, **35**, 3, 267 (1984).
6. Ciobanu D., Cecal Al., Rev. de chimie, **35**, 5, 420 (1984).

## DETERMINAREA UNOR CARACTERISTICI ALE ULEIULUI DE TALL BRUT

(Rezumat)

Se determină cele mai importante caracteristici fizico-chimice ale uleiului de tall brut separat la combinatul de fibre, celuloză și hirtie din orașul Dej. S-au supus la analiză probe din anii 1981, 1983 și 1985, constatându-se că nu apar diferențe importante privitoare la caracteristicile determinate, ele fiind invariabile în raport cu timpul de recoltare. Deoarece uleiul de tall are o compoziție chimică complexă, se propun câteva direcții de valorificare a acestui subprodus, care apare la fabricile de obținere a celulozei prin procedeul „sulfat”. Se recomandă separarea acestui produs la toate întreprinderile de specialitate.





## 2-HYDROXYKETONES

XVIII<sup>1)</sup>. SYNTHESIS OF SOME NEW 3, 3, 6, 7, 8-PENTASUBSTITUTED 4-CHROMANONES

BY

ALEXANDRU CAȘCAVAL

## 1. Introduction

The well-known Mannich reaction applied to some *ortho*-hydroxyphenylketones has been the subject of extensive synthetic effort in the last twenty years [2]...[5]. The most recent interesting result is reported by Werner [6] which converted 2'-hydroxyacetophenone in 3-dimethylaminomethyl-4-chromanone as a result from both a cyclocondensation and Mannich reaction in a „one-pot“ reaction (we have given the name Werner-Mannich reaction for this synthesis).

Our interest in the synthesis of various oxygen-containing heterocyclic compounds exhibiting physiological activities, led us to apply the Werner-Mannich reaction to some halogenated alkyl 2-hydroxyphenyl ketones and so we have developed a facile one-step synthesis of some new bis-Mannich bases as 3, 3, 6, 8-tetrasubstituted 4-chromanones [7]. More recent we have reported a new versatile (possible to be generalized) synthesis of some mono-Mannich bases of 2, 3, 3, 6, 8-pentasubstituted 4-chromanones in a Werner-Mannich reaction applied to a substituted 2'-hydroxychalcone [8].

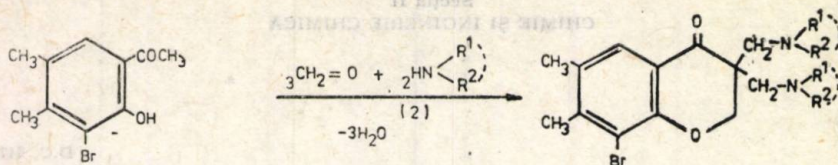
Kallay et al. [9] reported that some alkyl substituted 4-chromanones from natural sources exhibit physiological activity and more recent Ninagawa et al. [10] have found that two 2, 2, 5, 7, 8-pentasubstituted 4-chromanones are very useful as UV-absorbers.

## 2. Theoretical Considerations

Our recent results concerning the pharmacological screenings of some 3, 3, 6, 8-tetrasubstituted 4-chromanones [11] encouraged us to publish a very simple, one-step synthesis of some new 3, 3, 6, 7, 8-pentasubstituted 4-chromanones as bis-Mannich bases by both cyclocondensation and Mannich reaction: 3'-bromo-2'-hydroxy-4', 5'-dimethyl acetophenone (1) reacts with aqueous formaldehyde and cyclic secondary amines (2) to afford 3,3-cyclo-amino-methyl/-8-bromo-6,7-dimethyl-4-chromanones (3):

<sup>1)</sup> s. [1].



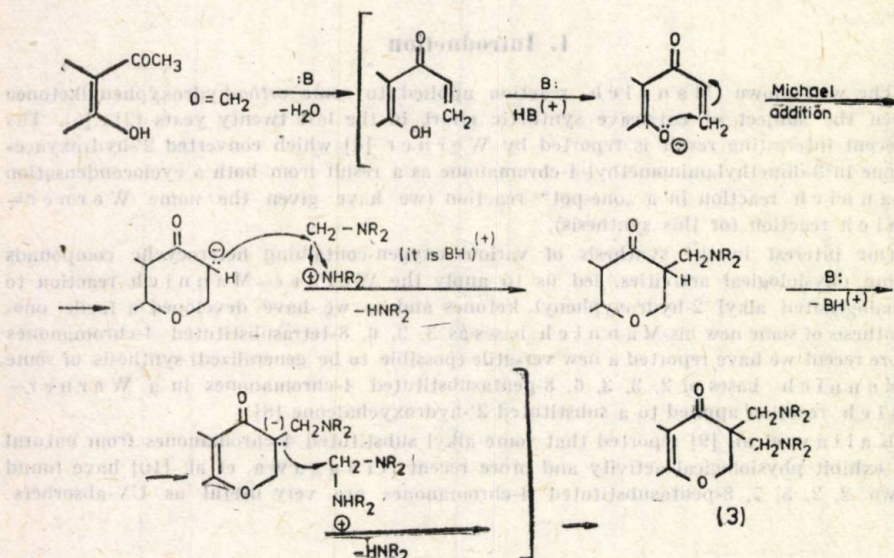


1)

(3)

| 23 | R <sup>1</sup>                                                          | R <sup>2</sup> |
|----|-------------------------------------------------------------------------|----------------|
| a  | - (CH <sub>2</sub> ) <sub>4</sub> -                                     |                |
| b  | - (CH <sub>2</sub> ) <sub>5</sub> -                                     |                |
| c  | -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> - |                |

The most probable mechanism of this Werner-Mannich reaction is given by the reactions :



In summary we have developed a simple one-step synthesis of some new bis-Mannich bases of 4-chromanones starting from *ortho*-hydroxyketones, formaldehyde and cyclic secondary amines with a great possibility of generalization of this type of Mannich reaction in basic medium; basic medium is given by methylene-bis-amine (CH<sub>2</sub>(NR<sub>2</sub>)<sub>2</sub>) which can be obtained by the reaction between formaldehyde and secondary amines.

Preliminary screening tests showed that the compounds (3) as dihydrochloride exhibit remarkable bactericidal and fungicidal activities [12].

The structures of compounds (1) and (3) were proven by microanalytical, I.R., and <sup>1</sup>H-N.M.R. - spectral data.



### 3. Experimental Part

#### 3.1. 3'-Bromo-2'-hydroxy-4',5'-dimethyl Acetophenone (1)

To a solution of 2'-hydroxy-4',5'-dimethylacetophenone [13] (16.5 g, 0.1 mol) in chloroform (100 ml) is added slow drop by drop bromine (16 g, 0.1 mol) at room temperature. The solution is allowed to stand at room temperature for 24 hours. The crude precipitate is recrystallized from ethanol; yield 76%; m.p. 105°...106°C.

|                                                        |            | C%    | H%   | Br%   |
|--------------------------------------------------------|------------|-------|------|-------|
| C <sub>10</sub> H <sub>11</sub> BrO <sub>2</sub> (243) | calculated | 49.38 | 4.53 | 32.92 |
|                                                        | found      | 49.50 | 4.62 | 33.11 |

I.R. (KBr):  $\nu$  2 900 (CH); 1 630 (CO) cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS<sub>int</sub>):  $\delta$ =2.2 (s, 3H, CH<sub>3</sub>-5'); 2.3 (s, 3H, CH<sub>3</sub>-4'); 2.5 (s, 3H, CH<sub>3</sub>-CO); 12.1 (s, 1H, OH - deuterable) ppm.

#### 3.1. 3.3-Bis(cycl-Aminomethyl)-8-bromo-6.7-dimethyl-4-chromanones (3); General Procedure

To a solution of acetophenone (1) (243 mg, 1 mmol) and the cyclic secondary amine (2) (technical grade, 2.5 mmol) in ethanol (25 ml) is added aqueous 30% formaldehyde (0.5 ml, 4 mmol) and the mixture is refluxed for 3 h. Cold water (100 ml) is then added and the product (3) is extracted with ether (2×25 ml). The extract is dried with sodium sulfate and evaporated to give crude product. For purification, products (3) are recrystallized from ethanol (Table 1).

Table 1  
Substituted 4-Chromanones (3) Prepared

| Product | Yield % | m.p. °C   | Molecular Formula <sup>a)</sup>                                          | I.R. (KBr) $\nu$ , [cm <sup>-1</sup> ]    | <sup>1</sup> H-N.M.R. (CDCl <sub>3</sub> /TMS <sub>int</sub> ) <sup>b)</sup> $\delta$ , [p.p.m.]                                                     |
|---------|---------|-----------|--------------------------------------------------------------------------|-------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3 a     | 83      | 111...112 | C <sub>21</sub> H <sub>29</sub> BrN <sub>2</sub> O <sub>2</sub><br>(421) | 2 900 (CH)<br>1 680 (CO)<br>1 240 (C-O-C) | 7.5 (s, 1H, H-5); 4.48 (s, 2H, CH <sub>2</sub> );<br>2.4-3.0 (m, 18H, 2CH <sub>3</sub> +6CH <sub>2</sub> N);<br>1.5-1.8 (m, 8H, 4CH <sub>2</sub> C). |
| 3 b     | 77      | 114...115 | C <sub>23</sub> H <sub>33</sub> BrN <sub>2</sub> O <sub>2</sub><br>(449) | 2 900 (CH)<br>1 685 (CO)<br>1 250 (C-O-C) | 7.5 (s, 1H, H-5); 4.5 (s, 2H, CH <sub>2</sub> );<br>2.5-3.0 (m, 18H, 2CH <sub>3</sub> +6CH <sub>2</sub> N);<br>1.5-2.0 (m, 12H, 6CH <sub>2</sub> C). |
| 3 c     | 60      | 123...124 | C <sub>21</sub> H <sub>29</sub> BrN <sub>2</sub> O <sub>4</sub><br>(453) | 2 900 (CH)<br>1 675 (CO)<br>1 230 (C-O-C) | 7.45 (s, 1H, H-5); 4.5 (s, 2H, CH <sub>2</sub> -2); 3.35-3.55 (t, 8H, 4CH <sub>2</sub> O)<br>2.2-2.9 (m, 18H, 2CH <sub>3</sub> +6CH <sub>2</sub> N). |

a) The microanalysis were in satisfactory agreement with the calculated values: C,  $\pm$ 0.25; H,  $\pm$ 0.20; N,  $\pm$ 0.25; Br,  $\pm$ 0.25.

b) Recorded on a JEOL instrument at 50°C and 60 MHz.

\* \* \*

The author is thankful to „Alexander von Humboldt-Stiftung“, Bonn, for providing a fellowship at the University of Freiburg i.Br., also Prof. Dr. Hans-Joachim Cantow and Prof. Dr. Gerhard Wegner for encouragements and generosity, BASF/Ludwigshafen (West-Germany) also Petrochemical Works, Borzesti, Romania, for the gift of several compounds.

Received, December 28, 1984

Polytechnic Institute, Jassy,  
Department of Organic and  
Macromolecular Chemistry and  
Technology



## REFERENCES

1. Cașcaval Al., *1,2-Hydroxyketones*. XVII, (private communication).
2. Котон М. М., Андреева И. В., Турбина А. И., Синяевский В. Г., ДАН СССР, **159**, 602 (1964).
3. Турбина А. И., Синяевский В. Т., Романкевич И., УХЖ, **31**, 85 (1965).
4. Tramontini M., *Synthesis*, 703 (1973).
5. Kabbe H. J., *Synthesis*, 886 (1978).
6. Werner W., *Arch. Pharm. (Weinheim Ger.)*, **309**, 1011 (1976).
7. Cașcaval A., *Synthesis*, 579 (1983).
8. Cașcaval Al., *Synthesis*, 277 (1984).
9. Kállay F., Janzsó G., Egyed I., Baitz-Gács E., in *Flavonoids and Bioflavonoids Current Research Trends*, edited by Farkas L., Gabor M., Kállay F., Akademiai Kiadó, Budapest, 1977, 235.
10. Ninagawa A., Iseki T., Matsuda H., *Makromol. Chem.*, **184**, 71 (1983).
11. Cașcaval Al., Mișcovici E., Chiorean V., *Romanian Patent (RSRP) 79907* (1982).
12. Cașcaval Al., Radu C., private communication.
13. v. Auwers K., Bundesmann H., Wieners F., *Liebigs Ann. Chem.*, **447**, 162 (1926).

## 2-HIDROXICETONE

## XVIII. Sinteza citorva noi 4-cromanone 3, 3, 6, 7, 8-pentasubstituie

## (Rezumat)

Se studiază extinderea reacției Mannich—Werner descrisă de noi în 1983 [7] constind în folosirea în calitate de *orto*-hidroxicetonă a produsului (1)-3'-brom-2'-hidroxi-4', 5'-dimetilacetofenona, care în reacție cu formaldehida (soluție apoasă) și aminele ciclice secundare (2) conduce cu randamente bune (între 60 și 83%) la bis-bazele Mannich—Werner (3 a...c). Se propune un mecanism al acestei reacții iar substanțele sintetizate sînt caracterizate din punct de vedere analitic și spectral (I.R., R.M.N.).

|   |   |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |     |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |



## DIRECT POLYCONDENSATION OF CYCLOALIPHATIC DICARBOXYLIC ACIDS WITH DIAMINES CATALYSED BY TRIPHENYL PHOSPHITE

BY

V. BULACOVSCI and MARIA GROVU-IVĂNOIU

### 1. Introduction

It is already known that phosphites, especially diphenyl and triaryl phosphites, react non-oxidatively with carboxylic acids in presence of pyridine to give acyl-oxy-N-phosphonium salt of pyridine accompanied by dephenoxylation, which produces the corresponding amides and esters on aminolysis and alcoholysis [1], [2]. The reaction promoted by triphenyl phosphite (TPP) and pyridine has been successfully applied to the direct polycondensation of *p*-aminobenzoic acid and isophthalic acid and diamines. High yields and high molecular weight polymers were obtained except when terephthalic acid was the monomer [3].

To overcome this difficulty it was suggested to realise these reactions in a mixed solvent of pyridine and N-methylpyrrolidone (NMP) or N,N-dimethylacetamide (DMAA) containing LiCl and CaCl<sub>2</sub> (separately or mixed) to increase the dissolution capacity of solvents [4]. Some considerations were also published concerning condition and order of introducing reactants and catalyst. More favourable results were obtained when inorganic salts were dissolved in presence of pyridine prior to use and the TPP in NMP was prewarmed.

In this paper we examine conditions for the synthesis of aromatic — cycloaliphatic polyamides by direct polycondensation of 1,2-cyclopropane- and 1-methyl-1,2-cyclopropanedicarboxylic acids (CPDA and MCPDA) with various aromatic diamines in presence of pyridine (Py) and TPP. The obtained polymers were characterised by spectral and thermal way.

### 2. Experimental Part

The cycloaliphatic dicarboxylic acids were prepared by the method mentioned in [5], [6]. Anhydrous CaCl<sub>2</sub> and LiCl were dried at 180°C for 8 h and 130°C for 4 h, respectively. The employed solvents were dried on CaH<sub>2</sub> and purified by vacuum distillation. Pyridine was dried on KOH and distilled over molecular sieves.

The polycondensation was carried out with magnetical stirring in a three neck flask, equipped with a reflux condenser, N<sub>2</sub> inlet tub and dropping funnel. The whole system was heated at 100°C for 2 h. The resulting polymer was ground in methanol, separated by filtration, washed with water and methanol and then dried in vacuum at 40°C. The viscosity of polymer sol-

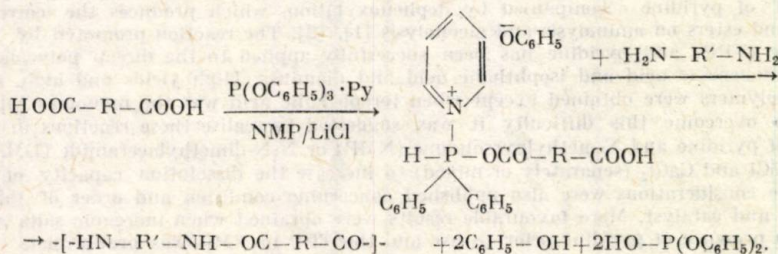


utions was measured on an Ubbelohde viscometer, in  $\text{H}_2\text{SO}_4$  (0.5 g/dL) at  $30^\circ\text{C}$ . The melting range was established on a hot-stage microscope in polarized light. Thermal analysis was run on a Paulik—Paulik—Erdey MOM, Budapest, apparatus, in a dynamical heating regime ( $7^\circ\text{C}/\text{min}$ ). The IR spectra (KBr pellets) were registered on a SPECORD — IR apparatus.

### 3. Results and Discussion

As a typical experiment of this investigation, a mixture of 0.65 g (5 mmol) CPDA, 0.541 g (5 mmol) *p*-phenyldiamine (*p*-PDA) and 2.1 g LiCl (or the preestablished quantities of  $\text{CaCl}_2$  and LiCl) is dissolved in 30 mL NMP and 10 mL pyridine on warming ( $50^\circ\text{C}$ ... $60^\circ\text{C}$ ). From the dropping funnel, a solution of TPP (3.1 g; 10 mmol) in 20 mL NMP preheated at approx.  $60^\circ\text{C}$  is added, then the temperature is raised at  $100^\circ\text{C}$  and maintained for 2 h. The catalytic presence of TPP favours, practically, a quantitative conversion of reactants; in equivalent amounts it brings also an important increase of the polymer viscosity.

The direct polycondensation of dicarboxylic acids with diamines promoted by phosphites, can be described by the following sequence of reactions [7]:



An important role is played by pyridine which improves the solubility of the salt, and solutions of higher concentration can be obtained. The better solubility might be due to the formation of a complex such as  $\text{CaCl}_2 \cdot n\text{Py}$  which may be readily soluble in NMP or DMAA. Pyridine enables also formation of the acyl-oxy-N-phosphonium intermediate, on what finally depend conversion and viscosity of the synthesised polymers.

The direct polycondensation of CPDA and *p*-PDA was carried out at  $100^\circ\text{C}$  for 2 h in a solution containing LiCl (2.1 g) initially dissolved in 50 mL NMP in the presence of various amounts of pyridine (Table 1). The viscosity of the resulting polymer increases with the amount of pyridine, showing better results for  $\text{NMP/Py} = 50/10$  [mL/mL] and  $\text{Py/LiCl} = 2.5$  ratios.

The polycondensation of CPDA and *p*-PDA was carried out also in various solvents containing LiCl in presence of pyridine. Among the solvents tested, NMP and DMAA proved to be more effective (Table 2). They readily dissolve the inorganic salt and resulted polymer, and possible, they influence the reactivity of the acyl-oxy-N-phosphonium intermediate. All reactions were carried out at constant monomer concentration and solvent/pyridine ratio.



Table 1

*Polycondensation of CPDA and p-PDA in NMP/Py Solution Containing LiCl*  
(time = 2 h ;  $T = 100^{\circ}\text{C}$ )

| Pyridine<br>mL | Py/LiCl<br>mol/mol | Conversion<br>% | $\eta_{inh}$ |
|----------------|--------------------|-----------------|--------------|
| 0              | 0                  | 96.1            | 0.015        |
| 4.1            | 1                  | 94.0            | 0.14         |
| 6.1            | 1.5                | 100.0           | 0.2          |
| 10.2           | 2.5                | 100.0           | 0.35         |

CPDA = *p*-PDA = 5 mmol ; NMP = 50 mL ;  $\text{P}(\text{OC}_6\text{H}_5)_3 = 10 \text{ mmol}$  ; LiCl = 2.1 g.

Table 2

*Effect of Solvent Nature on Polycondensation of CPDA and MCPDA with p-PDA*

| Dicarboxylic<br>Acid | Solvent | Conversion<br>% | $\eta_{inh}$ | Softening<br>range<br>$^{\circ}\text{C}$ |
|----------------------|---------|-----------------|--------------|------------------------------------------|
| CPDA                 | DMAA    | 100             | 0.33         | 300                                      |
| MCPDA                | DMAA    | 97.3            | 0.23         | 291...300                                |
| CPDA                 | NMP     | 100             | 0.35         | 300                                      |
| MCPDA                | NMP     | 100             | 0.19         | 251...260                                |
| CPDA                 | DMF     | 31.8            | 0.11         | —                                        |
| CPDA                 | DMSO    | 30.8            | 0.09         | —                                        |

Dicarboxylic acid = Diamine = 5 mmol ; Solvent = 50 mL ;  $\text{P}(\text{OC}_6\text{H}_5)_3 = 10 \text{ mmol}$  ; Py = 10 mL ;  $T = 100^{\circ}\text{C}$  ; time = 2 h ; LiCl = 2.1 g.

Nearly good yields were obtained in DMF and DMSO. Although LiCl was soluble in these solvents at the used concentration the obtained results are poor due, probable, to the lower solubility of the synthesised polyamides.

Table 3 retains some data concerning the influence of inorganic salts in the polycondensation process. Despite use of the same solvent composition and amount of metal salts, the reaction with the mixture of  $\text{CaCl}_2$  and LiCl dissolved in NMP/Py gave better results ( $\eta_{inh} = 0.42$ ). This phenomenon can be attributed to the increased solubility of the polymer and to an initial double salt complex  $\text{CaCl}_2 \cdot \text{LiCl} \cdot n\text{Py}$  which favors the polycondensation reaction [4].

Several aromatic — cycloaliphatic polyamides from CPDA, MCPDA and aromatic diamines were prepared by carrying out the reaction under the most favorable conditions for the reaction of CPDA and *p*-PDA (Table 4). Changing the diamine no significant effects were observed. However, it appears that substituted monomers give some higher molecular weight polyamides, and that polymers of MCPDA are of lower viscosity. Former aspects can be attributed to the increased solubility of the obtained polymer.



Table 3

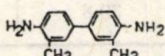
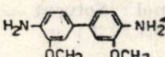
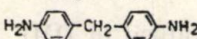
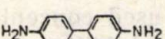
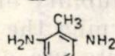
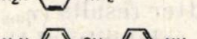
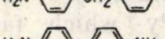
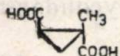
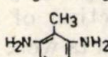
The Influence of the Nature and Salts Quantity upon the Polycondensation of CPDA and MCPDA with p-PDA in NMP/Py Solution

| Dicarboxylic acid | Inorganic salt          | Conversion % | $\eta_{inh}$ | Softening range °C |
|-------------------|-------------------------|--------------|--------------|--------------------|
| CPDA              | LiCl                    | 100          | 0.35         | 300                |
| CPDA              | CaCl <sub>2</sub>       | 98.5         | 0.12         | 295...300          |
| MCPDA             | CaCl <sub>2</sub>       | 98.9         | 0.11         | 282...290          |
| CPDA              | CaCl <sub>2</sub> /LiCl | 100          | 0.42         | 300                |
| MCPDA             | CaCl <sub>2</sub> /LiCl | 100          | 0.39         | 296...300          |

Dicarboxylic acid=Diamine=5 mmol ; NMP=50 mL ; Py/(CaCl<sub>2</sub>+LiCl)=2.5 mol/mol ; CaCl<sub>2</sub>/LiCl = 3 : 1 g/g ; Salt concentration = 4 % ; P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> = 10 mmol ; T = 100°C ; time = 2 h.

Table 4

Polyamides from CPDA, MCPDA and Several Diamines Prepared by Direct Polycondensation Technique in NMP/Py Solution Containing 4% w (CaCl<sub>2</sub>+LiCl)

| Dicarboxylic acid                                                                   | Diamine                                                                             | $\eta_{inh}$ | State of the system   |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------|-----------------------|
|  |   | 0.42         | Very viscous solution |
|                                                                                     |  | 0.48         | Very viscous solution |
|                                                                                     |  | 0.57         | Gel                   |
|                                                                                     |  | 0.23         | Gel                   |
|                                                                                     |  | 0.30         | Fluid gel             |
|                                                                                     |  | 0.29         | Consistent gel        |
|                                                                                     |  | 0.25         | Viscous solution      |
|                                                                                     |  | 0.226        | Viscous solution      |
|                                                                                     |  | 0.25         | Fluid gel             |
|                                                                                     |  | 0.28         | Viscous solution      |
|  |  | 0.18         | Gel                   |

Dicarboxylic acid=Diamine=5 mmol ; P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>=10 mmol ; NMP/Py=50/10 mL/mL ; CaCl<sub>2</sub>/LiCl = 3/1 g/g ; T = 100°C ; time = 2h.



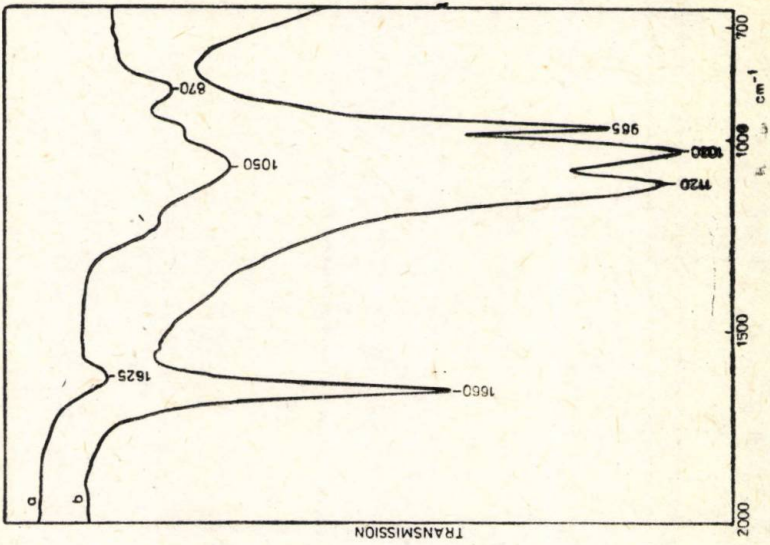


Fig. 2

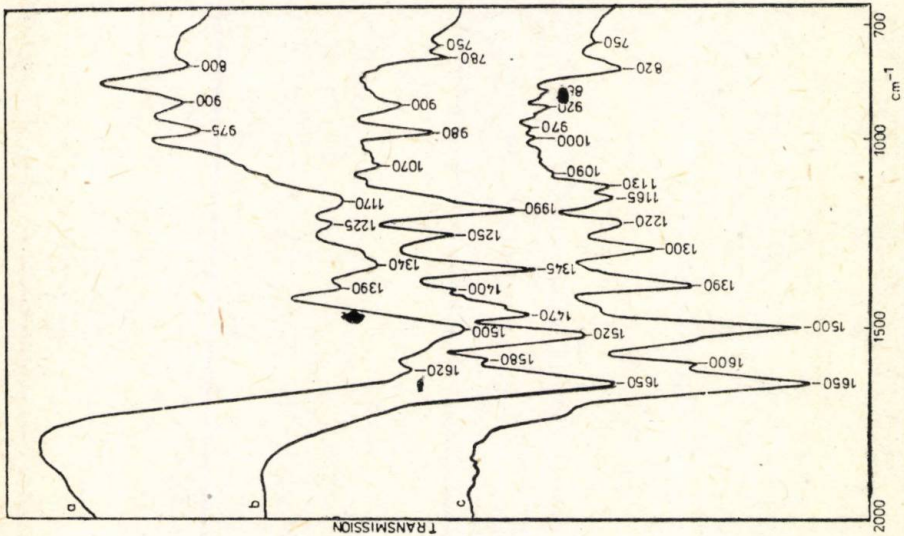


Fig. 1







In a similar manner we have prepared copolyamides of the *p*-amino-benzoic acid (*p*-ABA), CPDA and *p*-PDA (Table 5). Reaction proceeds almost quantitatively to products of high inherent viscosities and high melting points (over 300°C). These copolymers proved themselves to be also of remarkable thermostability. They lose less than 10% of their weight on heating at 375°...450°C.

Table 5

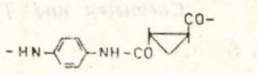
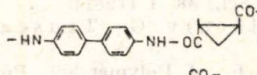
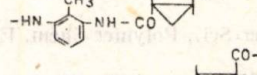
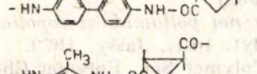
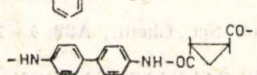
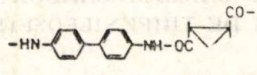
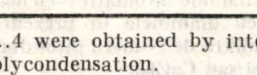
*Aromatic-Cycloaliphatic Copolyamides Prepared in NMP/Py Solution Containing 4% w (CaCl<sub>2</sub>+LiCl)*

| Comonomers, [mmol] |      |               | Conversion<br>% | $\eta_{inh}$ |
|--------------------|------|---------------|-----------------|--------------|
| <i>p</i> -ABA      | CPDA | <i>p</i> -PDA |                 |              |
| 20                 | —    | —             | 100             | 0.67         |
| 17                 | 1.5  | 1.5           | 99.1            | 1.02         |
| 14                 | 3.0  | 3.0           | 98.4            | 1.08         |
| 10                 | 5.0  | 5.0           | 98.8            | 1.10         |
| 5                  | 7.5  | 7.5           | 99.3            | 1.12         |

NMP = 130 mL; Pyridine = 20 mL; CaCl<sub>2</sub>/LiCl = 3/1 g/g; P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> = 20 mmol.

Table 6

*Thermal Behaviour of Polyamides with Cycloaliphatic Units in the Chain*

| No. | Polymer structure                                                                   | Reaction order    | <i>E<sub>a</sub></i> , [Kcal/mol] |                 |                 | Decomposition domain, °C            |
|-----|-------------------------------------------------------------------------------------|-------------------|-----------------------------------|-----------------|-----------------|-------------------------------------|
|     |                                                                                     |                   | I                                 | II              | III             |                                     |
| 1   |  | 1                 | —                                 | 67.06           | —               | 430...620                           |
| 2   |  | 2.4               | —                                 | 127.67          | —               | 480...630                           |
| 3   |  | 2.5               | —                                 | 49.63           | —               | 420...610                           |
| 4   |  | 0.08<br>1.7       | 21.02<br>—                        | —<br>29.08      | —<br>—          | 300...480<br>550...750              |
| 5   |  | 0.0<br>1.1        | 27.51<br>—                        | —<br>62.67      | —<br>—          | 130...210<br>550...670              |
| 6   |  | 1.6<br>1.5        | —<br>—                            | 63.72<br>—      | —<br>91.86      | 510...660<br>790...880              |
| 7   |  | 2.5<br>0.0<br>1.8 | 46.33<br>—<br>—                   | —<br>36.27<br>— | —<br>—<br>21.78 | 120...200<br>530...650<br>780...870 |

Polymers 1...4 were obtained by interfacial polycondensation; polymers 5...7 were obtained by direct polycondensation.



Spectral registrations of the synthesised polymers outline some characteristic IR-absorptions like those at  $1600\text{--}1650\text{ cm}^{-1}$  for amide I or  $1500\text{--}1520\text{ cm}^{-1}$ , for amide II structures (Fig. 1). For these polymers they are better revealed than in the products of the same structure but prepared by interfacial polycondensation [8].

The structural characteristics of the copolyamides are in good agreement with their composition. Cyclopropane unit in the macromolecular chain is outlined by  $965\text{ cm}^{-1}$  stretching vibration and amide I structure by  $1625\text{--}1660\text{ cm}^{-1}$  absorption (Fig. 2 b). There are no absorptions for amide II structure and, as a matter of fact, these spectra appear to be more simple.

To further understand the relationship of chemical structure to thermal stability, a thermogravimetric analysis of the synthesised products was undertaken. The results summarized in Table 6 show that the thermodegradative processes proceed in two or three steps. Also, the behaviour of cycloaliphatic—aromatic polyamides stands apart from other products having increased thermostability ( $400\text{--}450^\circ\text{C}$ ). High activation energies, especially for the symmetrical polymers, were calculated. For comparison, Table 6 includes also data concerning thermal behaviour of polyamides obtained by interfacial polycondensation technique.

#### 4. Conclusions

The obtained results indicate that direct polycondensation technique may be successfully used in the synthesis of aromatic—cycloaliphatic polyamides. Reaction proceeds with almost quantitative yields and to high molecular products, which show good thermal and chemical stability. By their properties the aromatic—cycloaliphatic polyamides are very close to the common aramides.

Received, April 23, 1987

Polylechnic Institute, Jassy,  
Department of  
Organic and Macromolecular  
Chemistry and Technology

#### REFERENCES

1. Yamazaki N., Higashi F., Adv. in Polymer Sci., **38**, 1 (1981).
2. Chiriac C., Grăescu D., Chiriac F., Răcaru G., Truscan I., Mat. plastice, **22**, 147 (1985).
3. Yamazaki N., Matsumoto M., Higashi F., J. Polymer Sci., Polymer Chem. Ed., **13**, 1378 (1975).
4. Higashi F., Ogata S. I., Aoki Y., J. Polymer Sci., Polymer Chem. Ed., **20**, 2081 (1982).
5. Mc. Coy E. L., J. Amer. Chem. Soc., **80**, 6568 (1958).
6. Bouchi E. Al., Cercetări în domeniul sintezei unor noi poliamide și copoliamide cu secvențe cicloalifatică în lanț. Ph. D. Diss., Polytechnic Inst., Jassy, 1979.
7. Higashi F., Goto M., Kakinoki H., J. Polymer Sci., Polymer Chem. Ed., **18**, 1711 (1980).
8. Bulacovschi V., Simionescu C., J. Macromol. Sci., Chem., **A22**, 5–7, 561 (1985).

#### POLICONDENSAREA DIRECTĂ A ACIZILOR CICLOALCANDICARBOXILICI CU DIAMINELE AROMATICE ÎN PREZENȚA DE TRIFENILFOSFIT (Rezumat)

Se studiază posibilitatea sintezei de poli- și copoliamide aromatic—cicloalifatică prin tehnica policondensării directe a acizilor dicarboxilici cu diaminele în prezență de trifenil fosfit. Reacția decurge cu randament cantitativ în soluție mixtă de N-metil pirolidonă și piridină în care s-a dizolvat în prealabil o sare anorganică (LiCl și/sau CaCl<sub>2</sub>).



# CONTRIBUTIONS TO THE SYNTHESIS, POLYMERIZATION AND COPOLYMERIZATION OF SOME *p*-SUBSTITUTED VINYLIC MONOMERS

BY

I. MAZILU, LUCIA TĂTARU, I. COCÎRLĂ, CAMELIA PETRESCU and  
TATIANA LIXANDRU

## 1. Introduction

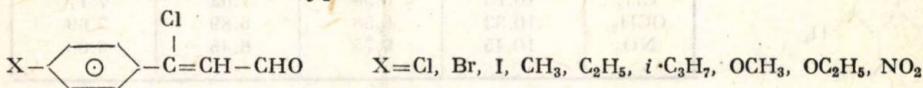
Polymers carrying reactive groups on the macromolecular chain have aroused a special interest, both from the theoretical and practical point of view. They may be used in analogous polymer reactions, on one side soluble, while on the other one, they may form tridimensional structures.

Literature data make mention of a series chloroformylated vinylic derivatives and of their polymerization [1]...[5].

The present paper studies the synthesis and characterization of some *p*-substituted chloroformylated compounds, their thermal polymerization and copolymerization, as well as the properties of the obtained compounds. Experimental data, correlated with LCAO—MO Hückel calculations, permitted certain considerations regarding the influence of the *p*-positioned substituents of the first and second order on the monomer reactivity, in the polymerization reaction.

## 2. Experimental Part

Monomers of the type



have been synthesized according to the method described in literature for similar compounds [3], [6]...[8], by the reaction of the acetylated derivatives with the Vilsmeier complex.

The reaction of thermal polymerization and copolymerization was performed in inert medium, in closed glass vials. Fractions soluble and insoluble in usual organic solvents have been obtained. Purification of the soluble fractions was achieved by their solving in benzene and by precipitation with acidified methanol, while the purification of the insoluble ones by repeated solvent washings, for the removal of monomers.



The IR spectra, in KBr tablets, have been registered with an UR-20 spectrophotometer, while the RMN spectra, with a Jeoltype equipment, by using  $\text{CDCl}_3$  as solvent and TMS as a standard.

The thermal stability of the monomers and polymers has been estimated through the thermograms registered with a derivatograph of the type MOM Budapest, J. Paulik — F. Paulik — L. Erdey.

The monomer reactivity has been estimated by LCAO — MO calculations, on an Iris-50 computer.

### 3. Results and Discussions

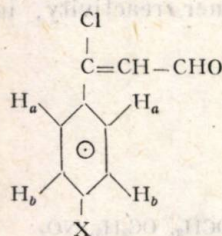
#### 3.1. Structure and Reactivity of Monomers

Chloroformylated vinylic derivatives have been characterized by elemental, spectral (IR and RMN) and thermodifferential analysis.

a) *The IR Spectra* of all monomers evidence characteristics bands of the  $\text{>C=O}$  groups, at  $1650\text{ cm}^{-1}$  ( $\text{X}=\text{Br}, \text{I}, \text{OCH}_3, \text{OC}_2\text{H}_5$ );  $1675\text{ cm}^{-1}$  ( $\text{X}=\text{Cl}, \text{CH}_3$ );  $1680\text{ cm}^{-1}$  ( $\text{X}=i\text{-C}_3\text{H}_7$ );  $1690\text{ cm}^{-1}$  ( $\text{X}=\text{NO}_2$ ) as well as of the *p*-substituted aromatic ring ( $700\text{--}900\text{ cm}^{-1}$ ). Absorptions caused by the ethylenic double bond and by the halogene fixed to the unsaturated carbon atom are superposed on the aromatic ring. The *p*-positioned substituents appear in the IR spectra at specific frequencies, namely:  $\nu_{\text{CH}_3, \text{sym.}}=2880\text{ cm}^{-1}$ ,  $\nu_{\text{CH}_3, \text{asym.}}=2913\text{ cm}^{-1}$ ,  $\nu_{\text{NO}_2, \text{sym.}}=1355\text{ cm}^{-1}$ ,  $\nu_{\text{NO}_2, \text{asym.}}=1525\text{ cm}^{-1}$ ; the ether link  $\text{C—O—C}$ ,  $1025\text{ cm}^{-1}$ .

The monomer structure is also confirmed by the values of the chemical shifts in RMN spectra:

$\delta$ , [ppm]



| X                | CHO   | =CH  | H <sub>a</sub> | H <sub>b</sub> |
|------------------|-------|------|----------------|----------------|
| Cl               | 10.29 | 6.63 | 7.68           | 7.50           |
| Br               | 10.28 | 6.62 | 7.56           | 7.80           |
| I                | 10.41 | 6.55 | 7.32           | 7.70           |
| CH <sub>3</sub>  | 10.15 | 6.58 | 7.62           | 7.17           |
| OCH <sub>3</sub> | 10.33 | 6.58 | 6.89           | 7.69           |
| NO <sub>2</sub>  | 10.45 | 6.75 | 8.45           | 8.00           |

b) *The Thermodifferential Analysis* shows a good thermal stability of the monomers up to  $100^\circ\text{C}$ , above which a two or three step degradation occurs.

At high temperatures ( $700^\circ, 800^\circ\text{C}$ ) the monomer decomposition is almost total.

For estimating the influence of the *p*-positioned substituent on the monomer reactivity in the polymerization reaction, the LCAO — MO Hückel method was applied. By performing the HMO calculations, the parameters listed in Fig. 1 have been used [9]...[11].



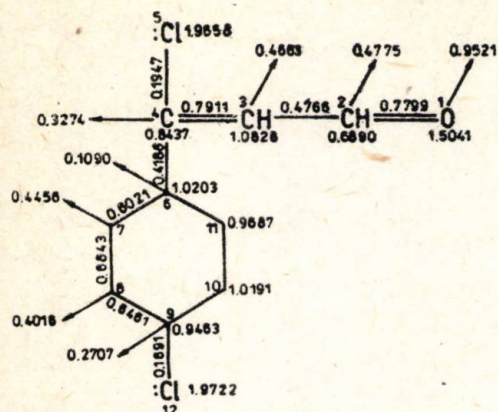


Fig. 2. — Molecular diagram of  $\alpha$ -chloro- $\beta$ -formyl-*p*-chlorostyrene.

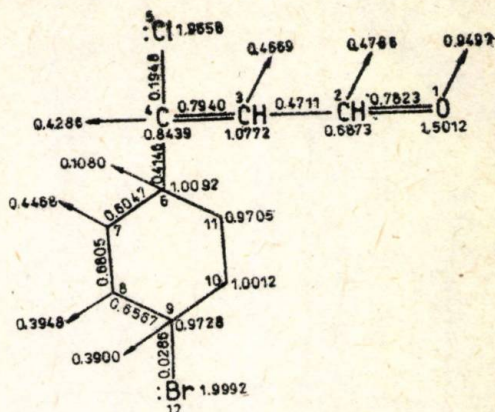


Fig. 3. — Molecular diagram of  $\alpha$ -chloro- $\beta$ -formyl-*p*-bromostyrene.

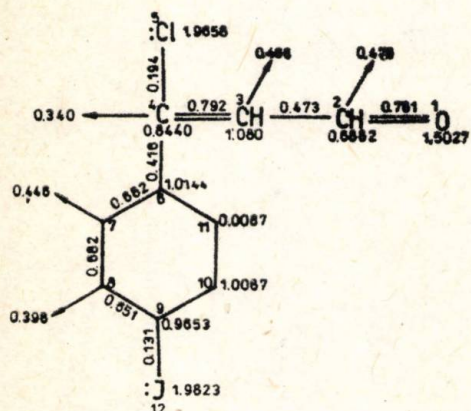


Fig. 4. — Molecular diagram of  $\alpha$ -chloro- $\beta$ -formyl-*p*-iodostyrene.

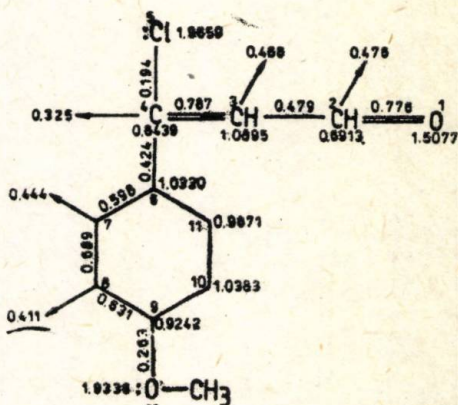


Fig. 5. — Molecular diagram of  $\alpha$ -chloro- $\beta$ -formyl-*p*-metoxystyrene.

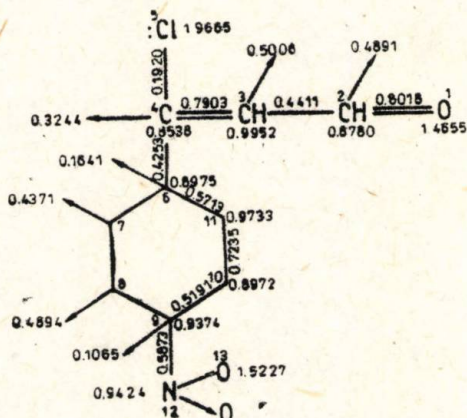


Fig. 6. — Molecular diagram of  $\alpha$ -chloro- $\beta$ -formyl-*p*-nitrostyrene.



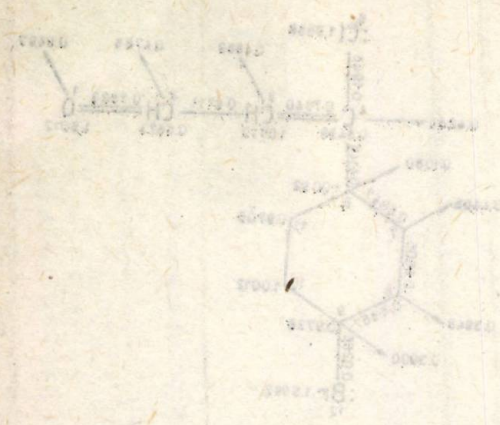


Fig. 1 - Molecular diagram of 2-chloro-5-formyl-3-methylstyrene

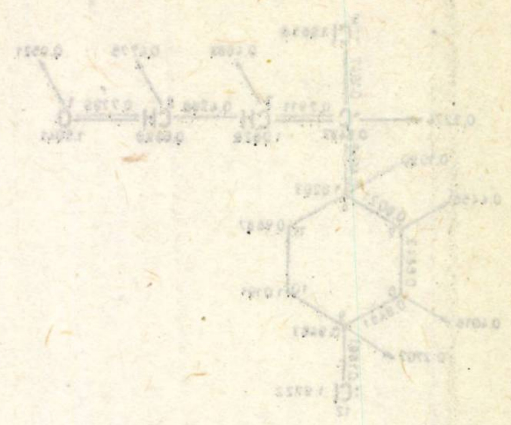


Fig. 2 - Molecular diagram of 2-chloro-5-formyl-3-methylstyrene

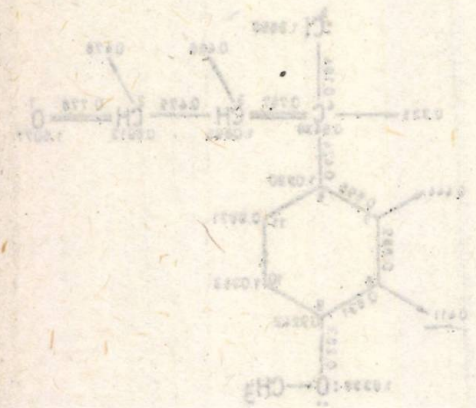


Fig. 3 - Molecular diagram of 2-chloro-5-formyl-3-methylstyrene

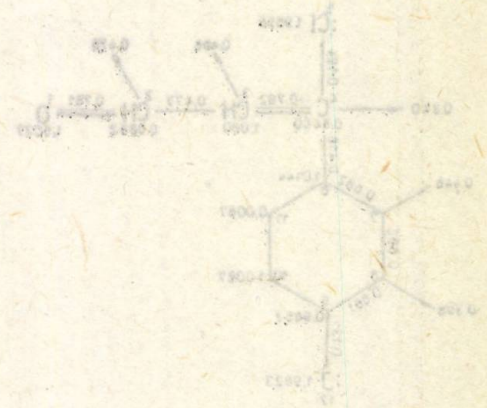


Fig. 4 - Molecular diagram of 2-chloro-5-formyl-3-methylstyrene

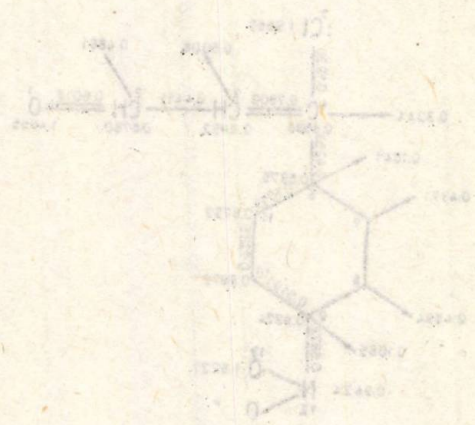
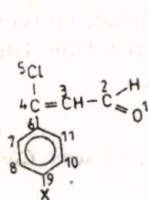


Fig. 5 - Molecular diagram of 2-chloro-5-formyl-3-methylstyrene

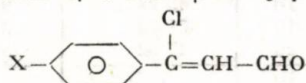


$$\begin{aligned}
 \alpha_{\dot{O}} &= \alpha + \beta & \beta_{C-Cl} &= 0.6\beta \\
 \alpha_{\ddot{O}} &= \alpha + 2\beta & \beta_{C-Br} &= 0.4\beta \\
 \alpha_{Cl} &= \alpha + 2.5\beta & \beta_{C-J} &= 0.3\beta \\
 \alpha_{Br} &= \alpha + 2.4\beta & \beta_{C-O} &= 0.8\beta \\
 \alpha_J &= \alpha + 1.2\beta & \beta_{C-NO_2} &= \beta \\
 \alpha_{C\equiv H_3} &= \alpha + 2\beta & \beta_{NO(NO_2)} &= \beta \\
 \alpha_{N(NO_2)} &= \alpha + \beta & \beta_{C-C\equiv H_3} &= 0.7\beta \\
 \alpha_{O(NO_2)} &= \alpha + 1.5\beta & \beta_{1,2} &= \beta_{3,4} = 1.1\beta \\
 & & \beta_{2,3} &= 0.9\beta
 \end{aligned}$$

Fig. 1. — Values of the  $\alpha$  (the Coulomb integral) and  $\beta$  (the resonance integral) parameters.

The obtained values are indicated in the molecular diagrams from Figs. 2 ... 6 and Table 1.

Table 1  
Molecular Characteristics of  $\alpha$ -Chloro- $\beta$ -Formyl- $p$ -Substituted Derivatives



| X                | Total energy<br>$E_{\pi}$ , [ $\beta$ ] | Resonance energy<br>$E_R$ , [ $\beta$ ] | $n_{\pi}$ | $E_R/n_{\pi}$ |
|------------------|-----------------------------------------|-----------------------------------------|-----------|---------------|
| H                | 19.5634                                 | 2.963                                   | 12        | 0.247         |
| Cl               | 24.6642                                 | 3.064                                   | 14        | 0.218         |
| Br               | 24.3663                                 | 2.966                                   | 14        | 0.212         |
| I                | 22.0030                                 | 3.403                                   | 14        | 0.243         |
| CH <sub>3</sub>  | 23.5436                                 | 2.943                                   | 12        | 0.210         |
| OCH <sub>3</sub> | 23.7720                                 | 3.172                                   | 14        | 0.226         |
| NO <sub>2</sub>  | 24.7919                                 | 3.692                                   | 14        | 0.263         |

$n$  — number of  $\pi$  electrons.

The  $E_R$  value represents the thermodynamic stability, while  $E_R/n$  — the chemical stability of the molecules [12].

By taking into account the values of the resonance energies and the chemical stability, one can estimate the influence of the substituents on the monomer reactivity, which increases in the order:



In the case of a radicalic process, present in thermal polymerization, the information from molecular diagrams evidence that, for all compounds, the radicalic attack (possibly, oxygen traces) begins at the C<sub>2</sub> atom ( $F_3 > F_4$ ; Figs. 2 ... 6).

### 3.2. Thermal Polymerization of $\alpha$ -Chloro- $\beta$ -Formyl- $p$ -X-Styrene

The influence of temperature and of the reaction time on the conversion and degree of polymerization has been studied; the data obtained are listed in Table 2.



As shown in Table 2, for the same reaction time, conversion increases with temperature. At the same temperature and reaction time, conversion

Table 2

*Experimental Data concerning the Thermal Polymerization and some Characteristics of the Obtained Products*

| X                               | Reaction temperature, [°C] | Time h | Conversion % | $\bar{p}$ | M.p. °C | Reference |
|---------------------------------|----------------------------|--------|--------------|-----------|---------|-----------|
| Cl                              | 180                        | 10     | 6.98         | 6         | 204     | [13]      |
|                                 | 200                        | 10     | 8.03         | 8         | 218     | [13]      |
|                                 | 230                        | 10     | 18.10        | 12        | 195     | [13]      |
|                                 | 300                        | 10     | 35.82        | 4         | 249     | [13]      |
|                                 | 300                        | 20     | 22.91        | 3         | 202     | [13]      |
| Br                              | 180                        | 10     | 35.08        | 7         | 230     | [13]      |
|                                 | 200                        | 10     | 43.79        | 6         | 250     | [13]      |
|                                 | 230                        | 10     | 43.98        | 9         | 266     | [13]      |
|                                 | 300                        | 10     | 51.72        | 3         | 294     | [13]      |
|                                 | 300                        | 20     | 47.52        | 3         | 284     | [13]      |
| I                               | 150                        | 10     | —*)          |           | —       | [15]      |
|                                 | 180                        | 10     | —*)          |           | —       | [15]      |
|                                 | 200                        | 10     | 25.5         |           | 256     | [15]      |
| CH <sub>3</sub>                 |                            |        | —*)          |           | —       | [15]      |
|                                 |                            |        | 47.7         |           | 256     | [15]      |
|                                 | 180                        | 10     | 18.5         | 6         | 256     | [14]      |
|                                 | 200                        | 10     | 27.8         | 7         | 210     | [14]      |
|                                 | 230                        | 10     | 31.8         | 14        | 256     | [14]      |
| C <sub>2</sub> H <sub>5</sub>   | 230                        | 20     | 33.8         |           |         | [14]      |
|                                 | 300                        | 10     | 44.5         |           | 300     | [14]      |
|                                 | 200                        | 10     | 10           |           | 195     |           |
|                                 | 230                        | 10     | 24           |           |         |           |
|                                 | 300                        | 10     | 54           |           | 300     |           |
| i-C <sub>3</sub> H <sub>7</sub> | 300                        | 20     | 37           |           | 200     |           |
|                                 | 200                        | 10     | 17           |           | 190     |           |
|                                 | 230                        | 10     | 19.5         |           |         |           |
|                                 | 300                        | 10     | 32.6         |           | 280     |           |
|                                 | 300                        | 20     | 29           |           | 300     |           |
| OCH <sub>3</sub>                | 150                        | 10     | 10.5*)       |           | 162     | [15]      |
|                                 |                            |        | 7            |           | 210     |           |
|                                 | 180                        | 10     | 9*)          |           | 165     |           |
|                                 |                            |        | 17           |           | 220     | [15]      |
|                                 | 200                        | 10     | —*)          |           | —       |           |
| OC <sub>2</sub> H <sub>5</sub>  |                            |        | 36.7         |           | 220     | [15]      |
|                                 | 150                        | 10     | —            |           | —       | [15]      |
|                                 | 180                        | 10     | 15*)         |           | 176     |           |
|                                 |                            |        | 18.5         |           | 235     | [15]      |
|                                 | 200                        | 10     | —*)          |           | —       | [15]      |
| NO <sub>2</sub>                 |                            |        | 34           |           | 235     | [15]      |
|                                 | 180                        | 10     | 68.3         |           | 185     | [14]      |
|                                 | 200                        | 10     | 79           |           | 185     | [14]      |
|                                 | 230                        | 10     | 76.4         |           |         | [14]      |
|                                 | 230                        | 20     | 77.62        |           |         | [14]      |
|                                 | 300                        | 10     | 59.6         |           |         | [14]      |

\*) soluble fraction.

increases in the series  $\text{Cl} < \text{Br} < \text{I}$  for  $\text{X} = \text{halogene}$  while for  $\text{X} = \text{alkyl}$ , it decreases with the size of the alkyl residue ( $\text{CH}_3 > \text{C}_2\text{H}_5 > i\text{-C}_3\text{H}_7$ ). The conversion variation for  $\text{OCH}_3$  and  $\text{OC}_2\text{H}_5$  is insignificant. The highest conversion has been registered for  $\text{X} = \text{NO}_2$ , which is in good agreement with the fact that the less reactive monomer (by LCAO—MO calculations) allows the formation of some tridimensional structures.

The average degree of polymerization, for soluble fractions, increases with the reaction temperature up to  $230^\circ\text{C}$ , gradually decreasing afterwards; at  $300^\circ\text{C}$  trimers or tetramers are being formed.

Doubling the time for the same reaction temperature leads to the decrease of the conversion and of the average degree of polymerization. Thus, the conclusion that may be drawn is that, for a longer reaction time, scission of the macromolecular chains occur.

In the case of  $\text{X} = \text{Cl}, \text{Br}, \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$  fractions soluble in most organic solvents have been only obtained, while insoluble products resulted with  $\text{X} = \text{NO}_2$ . In the case of  $\text{X} = \text{I}, \text{OCH}_3, \text{OC}_2\text{H}_5$  mixtures of soluble and insoluble fractions have resulted; the soluble fraction decreases with the increase of the insoluble one in the case of rising the reaction temperature.

a) *The Kinetics of the Polymerization Process* has been studied by the gravimetric method, for  $\text{X} = \text{CH}_3, i\text{-C}_3\text{H}_7, \text{Cl}, \text{Br}$ . Data obtained are listed in Table 3.

The graphical representation of the variation with time led to stright lines passing through the origin (Figs. 7, 8), which indicates a first order reaction [16].

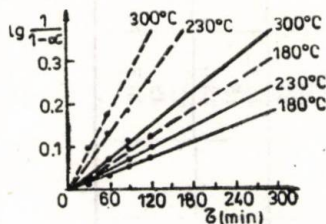


Fig. 7 a. — Variation of  $-\log [1/(1-\alpha)]$  vs. time, in the polymerization process of  $\alpha$ -chloro- $\beta$ -formyl- $p$ -X-styrene ( $\text{X} = \text{Cl}$  —;  $\text{X} = \text{Br}$  - -).

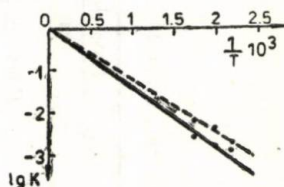


Fig. 7 b. — Variation of  $-\log K$  vs.  $1/T \times 10^3$  in polymerization process of  $\alpha$ -chloro- $\beta$ -formyl- $p$ -X-styrene ( $\text{X} = \text{Cl}$  —;  $\text{X} = \text{Br}$  - -).

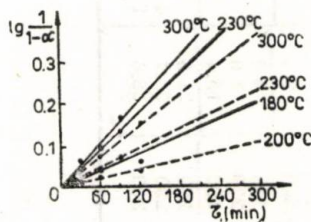


Fig. 8 a. — Variation of  $-\log [1/(1-\alpha)]$  vs. time in the polymerization of  $\alpha$ -chloro- $\beta$ -formyl- $p$ -X-styrene ( $\text{X} = \text{CH}_3$  —;  $\text{X} = i\text{-C}_3\text{H}_7$  - -).

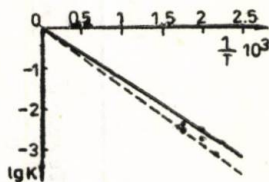


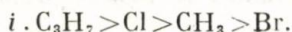
Fig. 8 b. — Variation of  $-\log K$  vs.  $1/T \times 10^3$  in polymerization process of  $\alpha$ -chloro- $\beta$ -formyl- $p$ -X-styrene ( $\text{X} = \text{CH}_3$  —;  $\text{X} = i\text{-C}_3\text{H}_7$  - -).



Table 3  
Kinetic Data concerning the Thermal Polymerization of  $\alpha$ -Chloro- $\beta$ -Formyl-p-X-Styrene

| X                                        | Temperature<br>°C | Time, [min.] |       |         |   |         |     |         |       | Rate<br>constant<br>$k$ , [s <sup>-1</sup> ] | Energy<br>activation<br>$E_a$<br>Kcal/mol |                       |       |
|------------------------------------------|-------------------|--------------|-------|---------|---|---------|-----|---------|-------|----------------------------------------------|-------------------------------------------|-----------------------|-------|
|                                          |                   | 30           |       | 60      |   | 90      |     | 120     |       |                                              |                                           | 300                   |       |
|                                          |                   | Conv. %      | M     | Conv. % | M | Conv. % | M   | Conv. % | M     |                                              |                                           | Conv. %               | M     |
| CH <sub>3</sub>                          | 180               | 17           |       | 8.2     |   | 24      |     | 14      | 620   | 27                                           | 382                                       | $1.52 \times 10^{-3}$ | 5.796 |
|                                          | 230               | 21           |       | 15      |   | 32      |     | 30      | 1 510 | 42                                           | 900                                       | $3.45 \times 10^{-3}$ |       |
|                                          | 300               | 14           |       | 22      |   | 56      | 935 | 52      | 841   | 53                                           | 835                                       | $4.61 \times 10^{-3}$ |       |
| <i>i</i> . C <sub>3</sub> H <sub>7</sub> | 180               | 3            |       |         |   | 3.3     |     | 8.6     | 1 018 |                                              |                                           | $7.67 \times 10^{-4}$ | 6.524 |
|                                          | 230               |              |       | 4       |   | 20      |     | 45      | 1 242 | 32                                           | 680                                       | $1.82 \times 10^{-3}$ |       |
|                                          | 300               | 7.4          |       | 5.8     |   | 53      |     | 48      | 1 379 | 54                                           | 790                                       | $2.88 \times 10^{-3}$ |       |
| Cl                                       | 180               | 4.6          |       | 15.6    |   | 13.1    |     | 17      | 1 380 | 19                                           | 1 300                                     | $1.47 \times 10^{-3}$ | 6.020 |
|                                          | 230               | 3.9          |       | 8.1     |   | 15      |     | 21.4    | 611   | 33                                           | 523                                       | $1.85 \times 10^{-3}$ |       |
|                                          | 300               | 15.4         |       | 24      |   | 23.6    |     | 24.3    | 1 380 | 33                                           | 1 910                                     | $3.06 \times 10^{-3}$ |       |
| Br                                       | 180               | 21.5         | 682   | 28.3    |   | 21      |     | 26.5    | 1 550 | 47                                           | 1 150                                     | $2.42 \times 10^{-3}$ | 5.460 |
|                                          | 230               | 33.7         | 4 300 | 29      |   | 42      |     | 43      | 2 860 | 47.6                                         | 1 020                                     | $5.37 \times 10^{-3}$ |       |
|                                          | 300               | 39.6         | 1 120 | 46      |   | 30.8    |     | 44.5    | 1 542 | 49                                           | 1 090                                     | $7.30 \times 10^{-3}$ |       |

In all situations considered, the rate constant varies insignificantly with temperature, except for  $X = i.C_3H_7$ ; in this case it increases with an order of magnitude, when temperature rises from 200° to 230°C. The activation energy decreases in the order:



### 3.3. Molecular Structure of Polymers

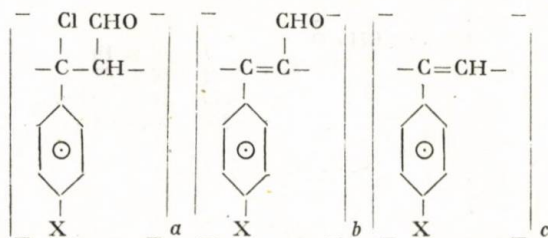
The structure of the products obtained by the polymerization of  $\alpha$ -chloro- $\beta$ -formyl- $p$ -X-styrene has been explained by IR spectra and elemental analysis.

Generally, IR spectra show absorption bands characteristic to monomers, yet of lower intensity:  $\delta_{p\text{-disubstituted aromatic CH ring}} = 700\ldots 900\text{ cm}^{-1}$ ,  $\nu_{C-C\text{ aromatic}} = 2970\ldots 3100\text{ cm}^{-1}$ . The absorptions caused by the olefinic link and by halogene superpose themselves on those of the aromatic ring.

The IR spectra of all synthesized products, at different temperatures and reaction times, are identical, which leads us to the conclusion that these factors do not influence the polymer structure. The soluble fractions proved to be oligomers with linear structure and degrees of polymerization ranging from 3 to 14. If a comparative analyze of the spectroscopic data and of the average degree of polymerization ( $\bar{p}$ ) is effectuated, there can be stated that at temperatures above 230°C, a competitive reaction of polymerization also occurs, yet, without affecting the products structure, the IR spectra being identical. Prolongation of the reaction time stimulates too the depolymerization process.

Results of elemental analysis and of spectral data evidence a dehydrohalogenation [17]...[19] or dehaloformylation occurring during the polymerization process. In the situation in which the dehydrohalogenation or dehaloformylation of the monomer [6], [8] proceeds at a higher ratio than the polymerization reaction, the acetylenic monomer, which may copolymerize with the vinylic monomer, is being formed.

Thus, in the process of thermal polymerization there take place several concurrent reactions which lead to a copolymer possessing diene or polyenic units on the macromolecular chain, for which we suggest the structure:



The presence of a system of double bonds conjugated on the macromolecular chain is confirmed too by the values of the electric conductivities, varying between  $10^{-14}$  and  $10^{-12}\text{ ohm}^{-1} \cdot \text{cm}^{-1}$ ; these values attest semiconducting properties of the synthesized products.



The thermodifferential analysis evidences that the thermal decomposition takes place in several steps, the products being stable up to approx. 250°C.

### 3.4. Copolymerization of $\alpha$ -Chloro- $\beta$ -Formyl-*p*-X-Styrene

The copolymerization of  $\alpha$ -chloro- $\beta$ -formyl-*p*-X-styrene has been studied for X=Cl, Br, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *i*.C<sub>3</sub>H<sub>7</sub>. Styrene and phenylacetylene were used as comonomers.

In all cases, copolymers soluble in usual solvents have been used. Special mentions must be made of the fact that, while the thermal polymerization of the chloroformylated monomers does not occur at 150°C, the copolymerization with styrene and phenylacetylene does. The influence of time and the reaction temperature is manifested on the conversion, as it is the case of the polymerization reaction [16].

### 3.5. The Molecular Structure of Copolymers

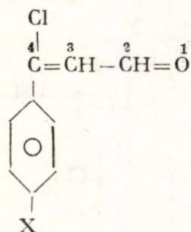
The copolymer molecular structure has been analyzed on the basis of the spectral data and the constants of copolymerization [16].

IR spectra show absorption bands characteristic to monomers:  $\nu_{C=O} = 1670...1680 \text{ cm}^{-1}$ ,  $\nu_{C-C \text{ aromatic}} = 1400...1610 \text{ cm}^{-1}$ ,  $\nu_{CH \text{ aromatic}} = 2930...3100 \text{ cm}^{-1}$ , *para*-disubstituted aromatic ring, 700...900  $\text{cm}^{-1}$ .

The copolymerization constants have been determined by LCAO-MO calculations, applying the relation:

$$-RT \ln r = (\Delta E_{rs})^1 - (\Delta E_{rs})^2,$$

where  $(\Delta E_{rs})^1$ ,  $(\Delta E_{rs})^2$  represent resonance energies for stabilizing the transition state between the radical and its monomer and, respectively, between the same radical and comonomer [19]. The  $\Delta E_{rs}$  values have been computed according to literature data [20], being expressed in  $-(\Delta\beta^2/\beta)$  units. The *r* and *s* indices in  $\Delta E_{rs}$  refer to the monomer atom and, respectively, to the radical one, participating in the transition state. The *I...IV* monomers take part in the transition state with atom 3, the electronic density on the marginal orbitals being maximum for these positions. In all these cases, atom 4 is radicalic:



- |     |                     |
|-----|---------------------|
| I   | X = Br              |
| II  | X = Cl              |
| III | X = NO <sub>2</sub> |
| IV  | X = CH <sub>3</sub> |

The copolymerization constants, *r*, calculated for 60°C (333° K) are indicated in Table 4. The molar ratio of the two monomers is not significant.

In the situations *A*<sub>1</sub>...*D*<sub>1</sub> the copolymer contains more styrene (more reactive), the monomers *I...IV* polymerizing themselves in the end. Phenylacetylene being less reactive than the monomers had in view, in cases *A*<sub>2</sub>, *B*<sub>2</sub>

Table 4  
Copolymerization Constants [16]

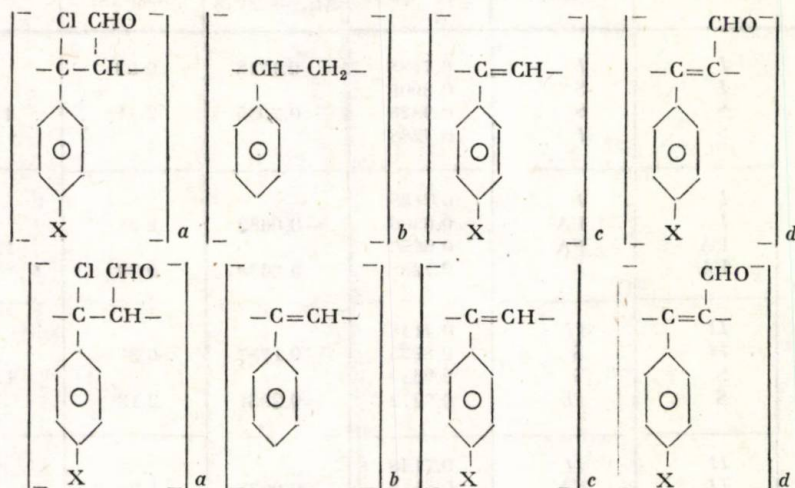
|       | Radical | Monomer | $\Delta E_{rs} = \Delta \beta^2 / \beta$ | Difference<br>$\Delta E_{rs} - \Delta \beta^2 / \beta$ | $r_{\text{computed}}$ | $r_1 r_2$ |
|-------|---------|---------|------------------------------------------|--------------------------------------------------------|-----------------------|-----------|
| $A_1$ | $I$     | $I$     | 0.7188                                   | 0.1718                                                 | 0.53                  | 1.11      |
|       | $I$     | $S$     | 0.8906                                   | -0.2035                                                | 2.11                  |           |
|       | $S$     | $S$     | 0.9323                                   |                                                        |                       |           |
|       | $S$     | $I$     | 0.7288                                   |                                                        |                       |           |
| $A_2$ | $I$     | $I$     | 0.7188                                   | -0.0682                                                | 1.28                  | 1.01      |
|       | $I$     | FA      | 0.6506                                   |                                                        | 0.0638                |           |
|       | FA      | FA      | 0.6650                                   | 0.79                                                   |                       |           |
|       | FA      | $I$     | 0.7288                                   |                                                        |                       |           |
| $B_1$ | $II$    | $II$    | 0.7148                                   | 0.1787                                                 | 0.51                  | 1.08      |
|       | $II$    | $S$     | 0.8935                                   |                                                        | 2.13                  |           |
|       | $S$     | $S$     | 0.9323                                   | -0.2051                                                |                       |           |
|       | $S$     | $II$    | 0.7272                                   |                                                        |                       |           |
| $B_2$ | $II$    | $II$    | 0.7148                                   | -0.0633                                                | 1.26                  | 1.001     |
|       | $II$    | FA      | 0.6515                                   |                                                        | 0.795                 |           |
|       | FA      | FA      | 0.6650                                   | 0.0622                                                 |                       |           |
|       | FA      | $II$    | 0.7272                                   |                                                        |                       |           |
| $C_1$ | $III$   | $III$   | 0.7116                                   | 0.1381                                                 | 0.60                  | 3.99      |
|       | $III$   | $S$     | 0.8497                                   |                                                        | 6.66                  |           |
|       | $S$     | $S$     | 0.9323                                   | -0.5140                                                |                       |           |
|       | $S$     | $III$   | 0.4183                                   |                                                        |                       |           |
| $C_2$ | $III$   | $III$   | 0.7116                                   | -0.0364                                                | 1.14                  | 2.82      |
|       | $III$   | FA      | 0.6752                                   |                                                        | 2.48                  |           |
|       | FA      | FA      | 0.6650                                   | -0.2467                                                |                       |           |
|       | FA      | $III$   | 0.4183                                   |                                                        |                       |           |
| $D_1$ | $IV$    | $IV$    | 0.7092                                   | 0.2008                                                 | 0.47                  | 1.005     |
|       | $IV$    | $S$     | 0.9100                                   |                                                        | 2.14                  |           |
|       | $S$     | $S$     | 0.9323                                   | -0.2065                                                |                       |           |
|       | $S$     | $IV$    | 0.7258                                   |                                                        |                       |           |
| $D_2$ | $IV$    | $IV$    | 0.7092                                   | -0.0514                                                | 1.21                  | 0.966     |
|       | $IV$    | FA      | 0.6578                                   |                                                        | 0.799                 |           |
|       | FA      | FA      | 0.6650                                   | 0.0608                                                 |                       |           |
|       | FA      | $IV$    | 0.7258                                   |                                                        |                       |           |

S — styrene ; FA — phenylacetylene.

and  $D_2$  the copolymer has a higher content of the monomers *I...IV*. In the case  $C_2$ , both copolymerization constants being higher than the unity, the homopolymerization tendency is stronger, the blockcopolymer being formed here of a mixture of the two homopolymers.



In most cases, copolymers show a statistical structure. On the macromolecular chain there exist systems of conjugated double bonds, as in the case of homopolymers, too, as a consequence of the dehydrohalogenation or dehaloformylation of the copolymer or of the chloroformylated vinylic mer:



Copolymers do not evidence semiconducting properties, which is probably due to the prevention of coplanarity of the units possessing conjugated double bonds.

#### 4. Conclusions

From the effectuated study the following conclusions regarding the synthesis, thermal polymerization and copolymerization with styrene and phenylacetylene of some *p*-disubstituted chloroformylated vinylic derivatives are established:

1. Monomers may be characterized by chemical, spectral (IR, RMN) and thermodifferential analyses.

2. Radical initiated thermal polymerization led to soluble ( $X=\text{Cl}$ ,  $\text{Br}$ ,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$ ) and insoluble ( $X=\text{NO}_2$ ) fractions, or to a mixture of soluble and insoluble products ( $X=\text{I}$ ,  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ ).

3. Conversion increases with temperature, up to  $230^\circ\text{C}$ , this limit exceeded, both conversion and the average degree of polymerization of the soluble compounds decreases, due to a depolymerization process. Prolongation of the reaction time over 10 hours promotes, too, the depolymerization process.

4. Kinetic data on the thermal polymerization show a first order reaction.

5. LCAO-MO calculations were undertaken, from which some conclusions on the monomer reactivity in the polymerization reaction have been drawn.

6. Soluble products are oligomers, possessing an average degree of polymerization (ranging from 3 to 14), a linear structure and conjugated units

on the macromolecular chain. Insoluble compounds have branched structures.

7. Correlation of analytical and spectral data indicated that the obtained products are copolymers, as a consequence of the dehydrohalogenation and dehydroformylation reaction of the polymer or of the monomer, which subsequently polymerizes with the vinylic mer.

8. Copolymerization of  $\alpha$ -chloro- $\beta$ -formyl-*p*-X-styrene with styrene and phenylacetylene has been studied, being established that over a certain temperature and reaction time, conversion decreases as a consequence of the concurrent reaction of depolymerization.

9. Calculation of the copolymerization constants, by the LCAO-MO method, permitted the estimation of the mers reactivity and, possibly, their sequence on the macromolecular chain.

10 Correlation of elemental analyses with spectral data and the values of the copolymerization constants attest that the synthesized products are copolymers having a linear structure and units with conjugated double bonds on the chain, possessing fragments with statistical and fragments with block structures.

Received, October 13, 1986

Polytechnic Institut, Jassy,  
Department of Organic and  
Macromolecular Chemistry  
and Technology

## REFERENCES

1. Юргова Г. А., Чюмаков У. В., Ежова Т. М., Джасин Л. Д., Сосин С. Л., Коршак В. В., Высокомол соед., **13**, 2 761 (1971).
2. Воронина М. А., Вишнякова Т. П., Таушкин Я. М., Божикова М. А., Альев Л. Н., Высокомол соед., **11**, 882 (1969).
3. Rosenblum M., Brown N., Porenmeier J., Applebaum M., J. Organometal. Chem., **6**, 2, 173 (1966).
4. Schlögl K., Steyer W., Monats., **96**, 1520 (1965).
5. Ликсандру Т., ЖОХ, **42**, 1991 (1972).
6. Bodendorf K., Mayer R., B., **98**, 3554 (1965).
7. Simionescu Cr., Dumitrescu Sv., Lixandru T., Dăringă M., Simionescu B., Vătă M., European Polymer J., **8**, 719 (1972).
8. Weissenfels M., Schurig H., Huhsam G., Z. Chem., **6**, 471 (1966).
9. Purcell W. P., Singer J. A., J. Chem. and Data., **12**, 235 (1967).
10. Стейтвизер Е., Теория молекулярных орбит (пер. с англ.). Изд. Мир., М., 1965, 126.
11. Хигаси К., Баба Н., Рембаум А., Квантовая органическая химия (пер. с англ.). Изд. Мир., М., 1967.
12. Pullman B., Pullman A., Quantum Biochemistry. J. Wiley & Sons, New York, London, 1963.
13. Lixandru T., Tătaru L., Mazilu I., Cocîrlă I., Rev. Roum. Chim., **20**, 129 (1975).
14. Lixandru T., Tătaru L., Mazilu I., Cocîrlă I., Bul. Inst. polit., Iași, **XXI** (XXV), 3-4, s. II, 69 (1975).
15. Mazilu I., Tătaru L., Cocîrlă I., Petrescu C., Lixandru T., Bul. Inst. polit., Iași, **XXXIV** (XXXVIII), 1-4, s. II (1988).
16. Lixandru T., Tătaru L., Mazilu I., Cocîrlă I., Bul. Inst. polit., Iași, **XXII** (XXVI), 1-2, s. II, 55 (1976).



17. Geddes W. C., European Polymer J., **3**, 733 (1967).
18. Hayashi K., Yonezawa T., Nagata C., Okamura S., Fukui K., J. Polymer. Sci., **20**, 537 (1956).
19. Stromberg R., Straus S., Achhammer B., J. Polymer Sci., **35**, 355 (1959).
20. Yonezawa S., Hayashi K., Nagata C., Okamura S., Fukui K., J. Polymer. Sci., **14**, 312 (1954).

## CONTRIBUȚII LA SINTEZA, POLIMERIZAREA ȘI COPOLIMERIZAREA UNOR MONOMERI VINILICI *p*-SUBSTITUIȚI

(Rezumat)

Se prezintă sinteza, polimerizarea termică și copolimerizarea cu stirenul și fenilacetilena a unor monomeri vinilici cloroformilați *p*-substituiți.

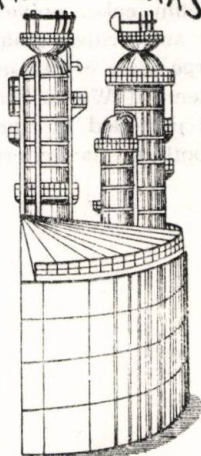
Influența substituentului asupra reactivității monomerilor a fost apreciată pe baza calculelor LCAO—MO și a datelor experimentale.

S-au obținut oligomeri solubili cu structură liniară și produși insolubili cu structură ramificată, având unități conjugate și grupe reactive pe catenă, cu proprietăți semiconductoare.

Studiul cinetic al polimerizării termice pune în evidență o reacție de ordinul întâi.

Datele analitice și spectrale ca și valorile constantelor de copolimerizare atestă pentru copolimerii cu stirenul și fenilacetilena o structură liniară cu unități conjugate pe catenă, prezentând fragmente cu structură bloc și fragmente cu structură statistică.

## PETROCHEMICAL WORKS BRAZI



### PRODUCES AND DELIVERS

- Comburents
- Aromatic hydrocarbons
- Polyisoprenic rubber
- Polybutadienic rubber
- Phenol
- Nonylphenol
- Ortosecundarbuthylphenol
- Acetone
- Low density polyethylene
- Phthalic and maleic anhydrides
- Choline chloride
- Dimethylterephthalate
- Ethanolamine
- Polyglycols 200 - 4000
- Monoethylene glicole



**MINISTRY OF CHEMICAL AND PETROCHEMICAL INDUSTRY  
INDUSTRIAL CENTRAL OF OIL DISTILLERIES AND PETROCHEMISTRY, BRAZIL**

Phone : 43121 ; Telex : 19343

---

**PETROCHEMICAL WORKS — BRAZIL**

The Petrochemical Works, Brazil, is a complex and modern unit of advanced technology for the oil processing and advanced chimization of the petroleum fractions, rendering profitable the base raw material.

The works produces a wide variety of petrochemical and oil products : comburents, fuels aromatic hidrocarbons, petroleum coke, polyethylene, ethylene oxide, dimethylterephthalate, maleic and phtholic anhydrides, ethanolamine, modifiers, synthetic rubbers, products which cover a large scale of utilizations.

The products manufactured by the Petrochemical Works, Brazil, are of high quality level according to the quality conditions provided in standards and common on the world market. They are destined both to the external and internal customers.



**SYNTHETIC FIBRE WORKS, IAȘI**, a modern unit of advanced technology, much ahead in Romania chemical industry, produces and deliveries a wide range of polyester fibers, yarns and sheets as well as equipments and spare parts for chemical and textile industry as it follows :

**1. Polyester synthetic fibers :**

- polyester fiber cotton type ;
- polyester fiber wool type (staple, top and tow) ;
- polyester fiber flax type ;
- polyester fiber high shrinkage.

**2. Polyester synthetic textile yarns :**

- polyester continuous filament textile twisted yarns for curtains and tissues ;
- polyester continuous filament drawn yarns for sewing thread ;
- polyester continuous filament textured yarn (semi-dull or bright, round or profiles, raw white or dyed) for knittings, tissues of cloths.

Colour card for dyed yarns includes about 100 shades classified in : light, medium and heavy shades.

**3. Polyester industrial yarns (drawn, twisted, plyed) for different technical end-uses.**

**4. Polyester sheets (transparent or light dull) for electrochemical industry.**

Besides its textile and chemical profile **SYNTHETIC FIBERS WORKS, IAȘI**, is also a manufacturer of equipments used in chemical and textile industries such as :

- equipments used for synthetic fiber production (technological lines) ;
- machinery for the chemical industry ;
- refrigeration plants ;
- precision conning machines according to the **SCHWEITER** licence ;
- inside rectification spindles ;
- yarn guides from sintered alumine ;
- metal structures ;
- different spare parts.

**The SYNTHETIC FIBRE WORKS, IAȘI**, exports its products by :

— **I.C.E. DANUBIANA, BUCHAREST**, service E. 9, telex 11184 for fibre and yarn.

— **I.C.E. MASINIEXPORTIMPORT, BUCHAREST**, telex 11206, for equipments and spare parts.

— **I.C.E. ELECTROEXPORTIMPORT, BUCHAREST**, service 44, telex 11388, for polyester sheets.

For any additional details please write directly to :

**COMBINATUL DE FIBRE SINTETICE, IAȘI**

29 Țuțora str., code 6600

Telex 022251



## ENTERPRISE FOR PROCESSING OF PLASTIC MATERIALS, IASI

In the past few years, the enterprise for processing plastic materials from Iași, has assimilate and processed new types of products from plastic materials, extending the scale of goods produced and processed polymers.

The traditional products are presented in the catalogue „Products Processed from Plastic Materials“ edited by the Ministry of Chemical and Petrochemical Industry in 1988 which can be obtained from the sale office of the enterprise.

Besides the mentioned goods in 1988 have been assimilated new products processed from poly(vinylchloride) :

a) Protective sheets for constructions.

b) Fireproof thermocontractible profiles.

c) Polyethylene products :

- Polyethylene aprons ;
- Protecting sheets with valves ;
- Flower pots ;
- Cloth covers ;
- High pressure tubings.

d) Polyurethane products :

- Valves ;
- Guiding rings ;
- Tighting cuffs ;
- Couplings.

e) Products from polypropilene :

- Cords and cables.

f) Products from PPAS :

- Profiles.

g) Products from ABS and polystyrene :

- Thermoformings from plates.

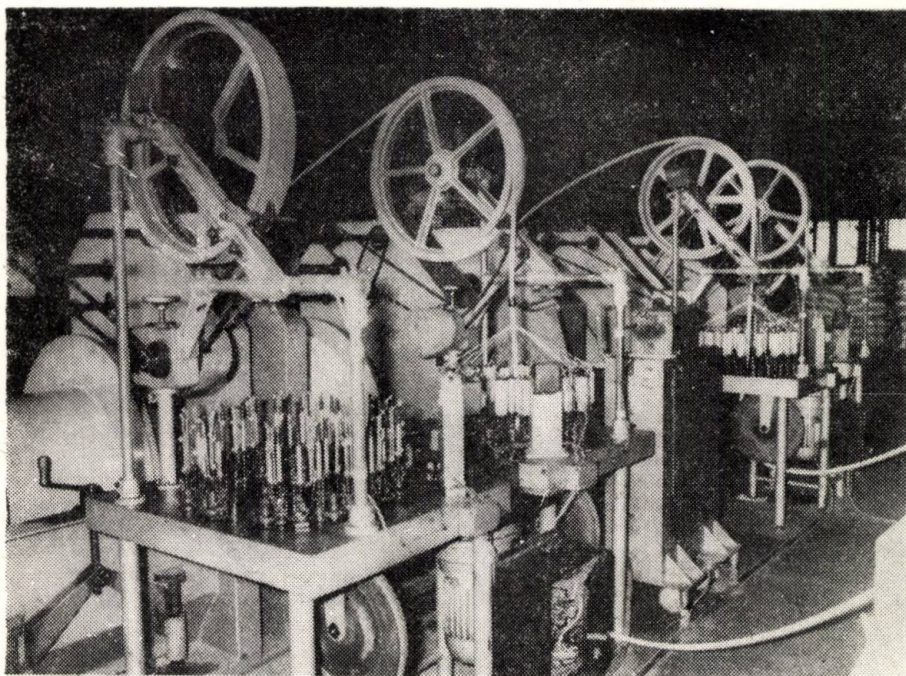
**SYNTHETIC FIBERS WORKS, SĂVINEȘTI**  
produces and delivers :

● *Synthetic Fibers and Yarns*

- Acrylic fibers Melana (R) ;
- Polyamidic fibers Relon (R) ;
- Polyamidic synthetic Yarns Relon (R) ;
- Polyamidic yarns carpet Relontex (R) ;
- Polyamidic technical and card yarns Relon (R) ;
- Brasnes cards.

● *Chemical Products*

- Caprolactam ;
- Adipic acid ;
- Tetrachlorethane ;
- Cyanuril chloride — Savicid (R) ;
- Dibenzyldiizocianate DBDI ;
- Polyethyleneglycole adipate PEGA ;
- Polyamidic grains for plastics Relon (R) ;
- Polyamidic plates and bars Relon (R).



● *Equipment and Spare Parts for Synthetic Fibers Industry*

- Complete lines for synthetic fiber drawing ;
- Spinning pumps for synthetic fibers ;
- Spinning nozzles for melt spinning ;
- Pressure pumps for cleanning vessels in chemical industry ;
- Yarns winding machines ;



- Sprindles for textile industry machines ;
- Cutting rolls for fibers ;
- Various spare parts used in chemical fibers industry.

**Producer : SYNTHETIC FIBERS SĂVINEȘTI, PIATRA NEAMȚ**

**TELEX 025221 — 222**

**TELEGRAPH CFS, SĂVINEȘTI**

**EXPORTERS :**

- Synthetic fibers and yarns :

**ICE DANUBIANA, BUCHAREST,**

**Bd. Republicii Nr. 10—12**

**Sector 4, BUCHAREST**

**TELEX 11184 danaz**

- Equipments and spare parts

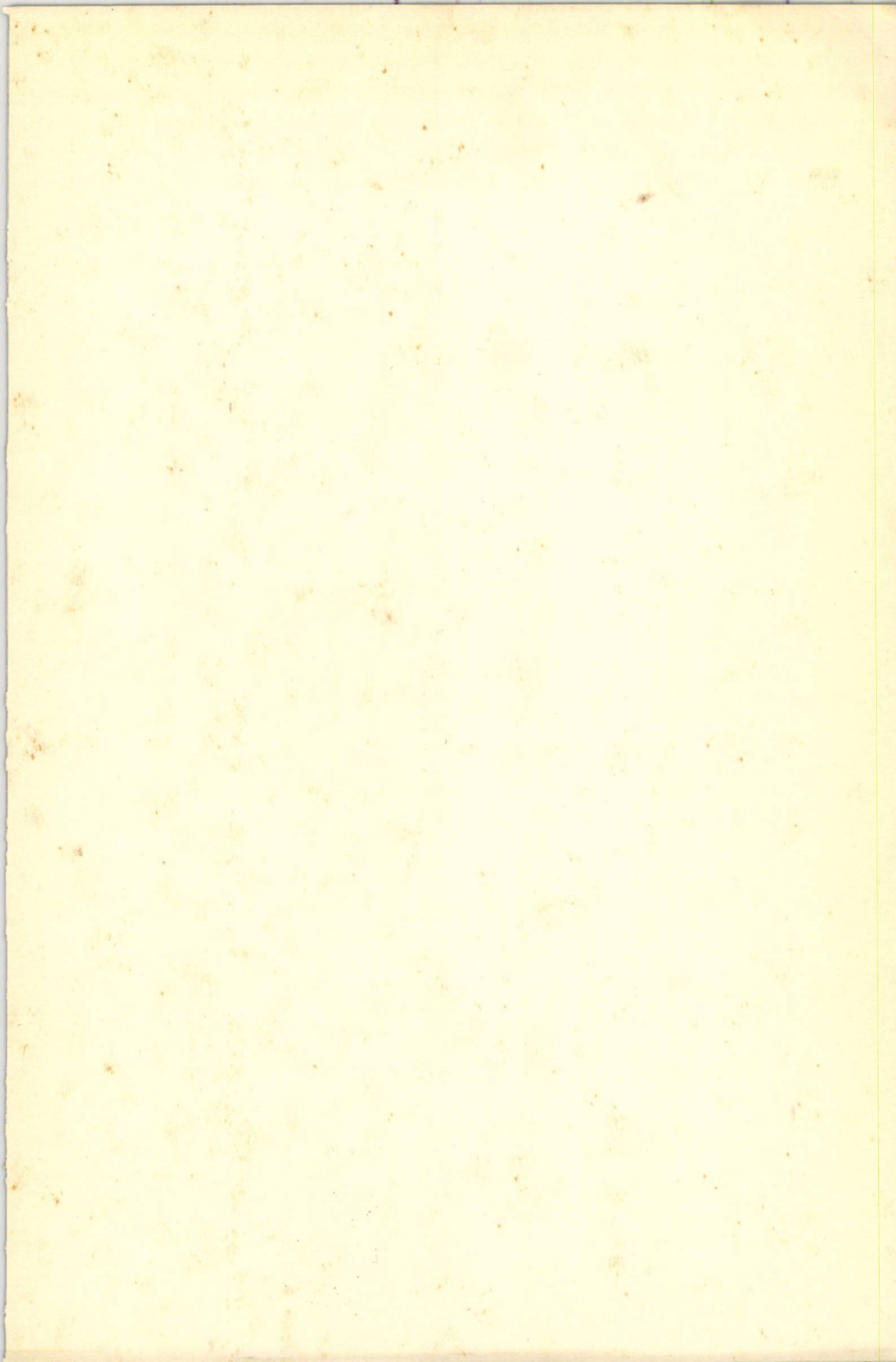
**ICE INDUSTRIALEXPORTIMPORT, BUCHAREST**

**Str. Scaune 1—3**

**Telex 10052—10930 /**

**POB 764**







1868 AUG 1/2

40822

F 1503/2

# BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI

Tomul XXXV (XXXIX)

Fasc. 3-4

Secția II

CHIMIE  
ȘI  
INGINERIE CHIMICĂ

1989



THE  
INSTITUTION  
OF THE  
FUTURE

THE  
FUTURE

THE  
FUTURE

THE  
FUTURE

THE  
FUTURE

THE  
FUTURE

THE  
FUTURE

# BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI



Tomul XXXV (XXXIX)

Fasc. 3-4

L. 041641

Secția II

CHIMIE  
ȘI  
INGINERIE CHIMICĂ

1989



### COLEGIUL DE REDACȚIE

Prof. dr. chim. **CAMELUȚA BELDIE** (președinte)  
Prof. dr. ing. **ADRIAN RADU**  
Prof. dr. ing. **M. GAFIȚANU**  
Conf. dr. ing. **D. LIUȚE**  
Prof. dr. doc. **D. MANGERON**  
Prof. dr. ing. **GH. MAXIM**  
Acad. prof. dr. doc. **CRISTOFOR SIMIONESCU**  
Prof. dr. doc. **GH. CHIRIȚA**  
Prof. dr. doc. **VALERIU BLIDARU**

*Această fascicolă a apărut și cu sprijinul material al comitetului sindical  
și consiliului U.A.S.C.R. al Institutului politehnic din Iași*

### COMITETUL DE REDACȚIE AL SECȚIEI

#### II. CHIMIE ȘI INGINERIE CHIMICA

Prof. dr. doc. **RADU TUDOSE**  
Prof. dr. **ANGELA POPA**  
Prof. dr. ing. **I. ROȘCA**  
Conf. dr. ing. **SPIRIDON OPREA**

### REDACȚIA

Prof. dr. doc. **D. MANGERON**  
(redactor responsabil)  
Prof. dr. ing. **HUGO ROSMAN**  
(secretar)  
Conf. dr. ing. **VICTOR BULACOVȘCHI**  
(redactor)  
**ECATERINA IRIMIEA**  
(tehnoredactor)

Secția II

**CHIMIE ȘI INGINERIE CHIMICĂ**

S U M A R

|                                                                                                                                                                                         | <u>Pag.</u> |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| I. ROȘCA, Sinteza și studiul polimerilor de coordinație ai Th (IV) și acidului difenilfosfinic (rusă, rez. rom.)                                                                        | 1           |
| A. BOLD, D. BEJAN, D. BÎLBĂ și L. TOFAN, Sorbția și separarea unor ioni metalici pe rășini schimbătoare de ioni modificate cu agenți sulfonați de chelatizare (engl., rez. rom.)        | 7           |
| V. DULMAN, AL. CECAL, T. ONOFREI și C. BURCOVEANU, Concentrarea toriului cu colectori microbiologici (engl., rez. rom.)                                                                 | 15          |
| AL. CECAL, Utilizarea diluției izotopice interne pentru determinarea solubilității unor sulfuri greu solubile (engl., rez. rom.)                                                        | 21          |
| I. M. POPA, D. HRIȚCU și GH. IONESCU, Aplicarea cromatografiei în faza lichidă de înaltă presiune la separarea produselor farmaceutice (engl., rez. rom.)                               | 27          |
| ȘT. IVĂȘCAN, F. BANDRABUR și M. APOSTOLESCU, Unele posibilități de reducere a consumurilor specifice de materiale și de energie în procesul de cromare electrolitică (engl., rez. rom.) | 31          |
| C. HAGIU și M. MICU, Noi sortimente de îngrășăminte din fosfoghips (engl., rez. rom.)                                                                                                   | 37          |
| S. PETRESCU și C. CALISTRU, Cercetarea cineticii procesului de obținere a sulfatului de potasiu prin dublu schimb din KCl și $(\text{NH}_4)_2\text{SO}_4$ (engl., rez. rom.)            | 41          |
| M. MACOVEANU și P. TALPALARU, Algoritm de optimizare de tip mixt (engl., rez. rom.)                                                                                                     | 47          |
| M. FOURAR și A. ALIANE (Algeria), Studiul unei coloane cu pulsații pentru extracție lichid-lichid (I) (franc., rez. rom.)                                                               | 53          |
| S. IFRIM, Cercetări privind comportarea linii drept componentă de cuplare (franc., rez. rom.)                                                                                           | 61          |
| C. LEONTE, E. CARP, S. DUMITRESCU, ȘT. CILIANU și R. BOZGA, Structuri amidice cu acțiune asupra sistemului nervos central (I) (franc., rez. rom.)                                       | 67          |
| E. CARP, C. LEONTE, S. DUMITRESCU, ȘT. CILIANU și R. BOZGA, Structuri amidice cu acțiune asupra sistemului nervos central (II) (franc., rez. rom.)                                      | 73          |
| AL. CAȘCAVAL, T. NICOLAESCU, ȘT. BIBIAN-CILIANU și C. V. ZĂNOAGĂ, Noi baze Mannich ale 3-nbutil-4-metilumbeliferonei (engl., rez. rom.)                                                 | 77          |
| V. ȘUNEL și C. CIUGUREANU, Noi derivații ai acidului L-asparagic cu activitate antitumorală potențială (engl., rez. rom.)                                                               | 81          |
| C. I. SIMIONESCU, V. BULACOVȘCHI și C. MIHĂILESCU, Polimerizarea acrilonitrilului inițiată de sistemul redox peroxidisulfat-sare di Bunte (engl., rez. rom.)                            | 87          |
| M. RUSU, Amestecuri de policlorură de vinil (IV) (engl., rez. rom.)                                                                                                                     | 93          |



Section II

CHEMISTRY AND CHEMICAL ENGINEERING

CONTENTS

|                                                                                                                                                                                                                  | Pp. |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| I. ROȘCA, Synthesis and Characterization of Th(IV) Coordinative Polymers Based on Diphenylphosphine (Russian, Romanian summary) . . . . .                                                                        | 1   |
| A. BOLD, D. BEJAN, D. BÎLBĂ and L. TOFAN, Sorption and Separation of some Metal Ions by Chelating Sulfonated Agent-Loaded Ion Exchangers (English, Romanian summary) . . . . .                                   | 7   |
| V. DULMAN, AL. CECAL, T. ONOFREI and C. BURCOVEANU, The Concentration of Thorium by Means of Microbiological Collectors (English, Romanian summary) . . . . .                                                    | 15  |
| AL. CECAL, The Use of Internal Isotopic Dilution for the Solubility Determination of certain Hard Soluble Sulphides (English, Romanian summary) . . . . .                                                        | 21  |
| I. M. POPA, D. HRÎTCU and GH. IONESCU, Application of Liquid High Pressure Chromatography in the Separation of Pharmaceutical Products (English, Romanian summary) . . . . .                                     | 27  |
| ȘT. IVĂȘCAN, F. BANDRABUR and M. APOSTOLESCU, Some Possibilities of Reducing the Material and Power Consumptions in the Process of Chrome Electrodeposition (English, Romanian summary) . . . . .                | 31  |
| C. HAGIU and M. MICU, New Sorts of Phosphogypsum Fertilizers (English, Romanian summary) . . . . .                                                                                                               | 37  |
| S. PETRESCU and C. CALISTRU, Investigations about the Kinetics of the Obtaining Process of Potassium Sulphate by Double Exchange from KCl and $(\text{NH}_4)_2\text{SO}_4$ (English, Romanian summary) . . . . . | 41  |
| M. MACOVEANU and P. TALPALARU, Mixed-Type Optimizing Algorithm (English, Romanian summary) . . . . .                                                                                                             | 47  |
| M. FOURAR et A. ALIANE (Algérie), Étude d'une colonne à pulsations pour l'extraction liquide-liquide (I), (French, Romanian summary) . . . . .                                                                   | 53  |
| S. IFRIM, Investigations concernant le comportement de la laine comme composant de copulation (French, Romanian summary) . . . . .                                                                               | 61  |
| C. LEONTE, E. CARP, S. DUMITRESCU, ȘT. CILIANU et R. BOZGA, Structures amidiques avec action sur le système nerveux central (I) (French, Romanian summary) . . . . .                                             | 67  |
| E. CARP, C. LEONTE, S. DUMITRESCU, ȘT. CILIANU et R. BOZGA, Structures amidiques avec action sur le système nerveux central (II) (French, Romanian summary) . . . . .                                            | 73  |
| AL. CAȘCAVAL, T. NICOLAESCU, ȘT. BIBIAN-CILIANU and C. V. ZĂNOAGĂ, New Mannich Bases of 3-nButhyl-4-methylumbelliferone (English, Romanian summary) . . . . .                                                    | 77  |
| V. ȘUNEL and C. CIUGUREANU, New Derivatives of L-asparagic Acid with Potential Antitumoral Activity (English, Romanian summary) . . . . .                                                                        | 81  |
| C. I. SIMIONESCU, V. BULACOVSCI and C. MIHĂILESCU, Polymerization of Acrylonitrile Initiated by the Peroxydisulfate-di Bunte Salt Redox Couple (English, Romanian summary) . . . . .                             | 87  |
| M. RUSU, Poly(vinil chloride) blends (IV) (English, Romanian summary) . . . . .                                                                                                                                  | 93  |



Секция II

ХИМИЯ И ХИМИЧЕСКАЯ ПРОМЫШЛЕННОСТЬ

СОДЕРЖАНИЕ

|                                                                                                                                                                                        | Стр. |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| И. РОШКА, Синтез и исследование координационных полимеров Th(IV) на основе дифенилфосфиновой кислоты (русс., рез. рум.) . . . . .                                                      | 1    |
| А. БОЛД, Д. БЕЖАН, Д. БЫЛБЭ и Л. ТОФАН, Сорбция и разделение металлических ионов модифицированным ионообменником с реагентами содержащих сульфогруппы (англ., рез. рум.) . . . . .     | 7    |
| В.ДУЛМАН, АЛ. ЧЕКАЛ, Т. ОНОФРЕЙ и К. БУРКОВЯНУ, Концентрирование торя с помощью микробиологических коллекторами (англ., рез. рум.) . . . . .                                           | 15   |
| АЛ. ЧЕКАЛ, Использование внутреннего изотопического распределения растворимости некоторых трудно-растворимых сульфидов (англ., рез. рум.) . . . . .                                    | 21   |
| И. М. ПОПА, Д. ХРИЦКУ и Г. ИОНЕСКУ, Применение жидкостной хроматографии высокого давления для разделения фармацевтических продуктов (англ., рез. рум.) . . . . .                       | 27   |
| Ш. ИВЭШКАН, Ф. БАНДРАБУР и М. АПОСТОЛЕСКУ, Некоторые способности снижения удельных расходов матерялов и энергии в процессе электролитической хромирования (англ., рез. рум.) . . . . . | 31   |
| К. ХАДЖИУ и М. МИКУ, Новые удобрение из фосфогипс (англ., рез. рум.) . . . . .                                                                                                         | 37   |
| С. ПЕТРЕСКУ и К. КАЛИСТРУ, Исследование кинетики процесса получения сульфата калия двойным обменом KCl и $(\text{NH}_4)_2\text{SO}_4$ (англ., рез. рум.) . . . . .                     | 41   |
| М. МАКОВЯНУ и П. ТАЛПАЛАРУ, Смешанным алгоритм оптимизации (англ., рез. рум.) . . . . .                                                                                                | 47   |
| М. ФУРАР и А. АЛИАНЕ (Алжыр), Изучение жидкостной пульсирующей экстракционной колонны (I) (франц., рез. рум.) . . . . .                                                                | 53   |
| С. ИФРИМ, Исследования относительно применения шерсти как азосочетания компонент (франц., рез. рум.) . . . . .                                                                         | 61   |
| К. ЛЕОНТЕ, Э. КАРП, С. ДУМИТРЕСКУ, Ш. ЧЛИИАНУ и Р. БОЗГА, Амидные соединения с действием на центральную нервную систему (I) (франц., рез. рум.) . . . . .                              | 67   |
| Э. КАРП, К. ЛЕОНТЕ, С. ДУМИТРЕСКУ, Ш. ЧИЛИАНУ и Р. БОЗГА, Амидные соединения с действием на центральную нервную систему (II) (франц., рез. рум.) . . . . .                             | 73   |
| АЛ. КАШКАВАЛ, Т. НИКОЛАЕСКУ, Ш. БИБИАН-ЧИЛИАНУ и К. В. ЗЭНОАГЭ, Новые Манних основания от 3-нбутил-4-метилумбеллифероны (англ., рез. рум.) . . . . .                                   | 77   |
| В.ШУНЕЛ и К. ЧЮГУРЯНУ, Новые производные L-аспаражик кислоты с потенциальным противотуморальным действием (англ., рез. рум.) . . . . .                                                 | 81   |
| К. И. СИМИОНЕСКУ, В. БУЛАКОВСКИЙ и К. МИХЭИЛЕСКУ, Редокс полимеризация акрилонитрила в присутствии системы персульфат-соль ди-Бунте (англ., рез. рум.) . . . . .                       | 87   |
| М. РУСУ, Поливинилхлоридные композиции (IV) (англ., рез. рум.) . . . . .                                                                                                               | 93   |





УДК 54-92; 546.843; 547.63

## СИНТЕЗ И ИССЛЕДОВАНИЕ КООРДИНАЦИОННЫХ ПОЛИМЕРОВ Th(IV) НА ОСНОВЕ ДИФЕНИЛФОСФИНОВОЙ КИСЛОТЫ

И. РОШКА

### 1. Введение

В последнее время с целью получения новых термостойких материалов проводятся широкие исследования различных координационных полимеров [1]...[10]. Так получены многочисленные координационные полимеры на основе диорганосфосфиновых кислот и различных катионов переходных металлов [1]...[11].

Особенно интересными являются полимеры диорганосфосфиновой кислоты с различными катионами, полученные Коршаком и сотр. [5], [6]; эти полимеры разлагаются при температурах выше 350°C.

Недавно синтезированы и исследованы новые координационные полимеры  $UO_2^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$ ,  $Ce^{3+}$  с дифенил- и диалкилфосфиновыми кислотами и с соответствующими тиокислотами [7]...[11].

В настоящей работе получены и исследованы некоторые координационные полимеры  $Th^{4+}$  на основе дифенилфосфиновой кислоты.

### 2. Экспериментальная часть

Дифенилфосфиновую кислоту  $(C_6H_5)_2PO_2H$ , получали по описанным ранее методам [12], дважды перекристаллизовали из этанола т. пл. 192°, 5...193,5°C (по [12] т. пл. 190°...192°C).

Ацетилацетонат  $Th(IV)$ ,  $Th(C_5H_7O_2)_4$ , получали по описанной ранее методике [9] из ацетилацетона и  $Th(OH)_4$ .

Общим методом получения гидроокисей  $Th(OH)_4$  является взаимодействие раствора  $ThCl_4$  с щелочами.

Синтез координационных полимеров производили поликонденсацией в расплаве, в органических растворителях, в обычной и инертной атмосферах.

Поликонденсация в расплаве 0,2 моля дифенилфосфиновой кислоты и 0,1 моля свежесинтезированной гидроокиси  $Th(IV)$  тщательно измельчивали и помещали в колбу, снабженную прямым холодильником с градуированным приёмником и трубкой для ввода азота. В течение часа температуру постепенно поднимали до 195°... 200°C и реакционную смесь выдерживали при этой температуре 2 ч. Затем смесь охлаждали, снова тщательно измельчивали и грели в течение двух часов, повышая температуру до 195°... 200°C. Полученные полимеры экстрагировали ацетоном и этанолом в аппарате Сокслета. Так синтезирован полимер типа I.

Аналогично получали полимеры II из 0,2 моля дифенилфосфиновой кислоты и 0,1 моля ацетилацетоната  $Th(IV)$  и III из 0,1 моля ацетилацетоната  $Th(IV)$  и 0,4 моля  $(C_6H_5)_2PO_2H$ .



Выход полимеров : 96...98% ; они частично растворимы в бензоле, хлороформе, спирте и др.

Поликонденсация в органических растворителях 0,1 моля ацетилацетоната Th(IV) и 250 мл бензола, толуола, этанола или бутанола, 0,2 моля дифенилфосфиновой кислоты, помещали в трехгорлую колбу, снабженную прямым холодильником, мешалкой и капиларом для ввода азота. Длительность реакций — 4 ч. Реакцию заканчивали после прекращения выделения ацетилацетона. Осадок отфильтровывали, промывали этанолом и экстрагировали в аппарате Сокслета этанолом. Состав этого соединения соответствует составу полимера II.

Аналогично получали и дифенилфосфинат Th(IV) из 0,1 моля дифенилфосфиновой кислоты и 0,025 моля ацетилацетоната Th(IV), соответствующий составу полимера III.

Осадок нерастворимого полимера промывали несколько раз этанолом и сушили до постоянного веса при 105°C. Растворимую фракцию полимера выделяли испарением растворителей и сушили до постоянного веса. Выход полимеров 90...95%. Эти полимеры частично растворимы в бензоле, хлороформе, спирте и других растворителях и имеют те же самые составы, что и соответствующие полимеры, полученные в расплаве. Все эти синтетизированные соединения — порошок белого цвета.

### 3. Полученные данные

Молекулярная масса растворимых фракций полимеров была определена эбуллиоскопическим методом в бензоле (табл. 1).

Наилучшие результаты были получены при взаимодействии дифенилфосфиновой кислоты и ацетилацетонатом Th(IV) или гидроокисью Th(IV). Элементный состав растворимых и нерастворимых идентичен (табл. 1).

Таблица 1

*Элементный состав и молекулярная масса растворимых фракций полимеров*

| Поли-<br>мер | Вычислено, [%] |      |       |       | Найдено [%] |      |       |      | М     |
|--------------|----------------|------|-------|-------|-------------|------|-------|------|-------|
|              | C              | H    | P     | Th    | C           | H    | P     | Th   |       |
| I            | 41,14          | 3,14 | 8,85  | 33,14 | 42,02       | 3,81 | 9,01  | 33,4 | 5 020 |
| II           | 47,22          | 4,16 | 7,17  | 26,85 | 48,11       | 4,72 | 7,12  | 29,0 | 9 080 |
| III          | 52,36          | 3,63 | 11,27 | 21,28 | 52,88       | 3,96 | 11,76 | 21,6 | 1 200 |

Результаты гель - хроматографического фракционирования координационных полимеров, осуществленного на приборе типа „Watter“ (наполнитель — стирекс, элюент — циклогексанон) показывают (рис. 1), что эти полимеры имеют различающееся ММР.

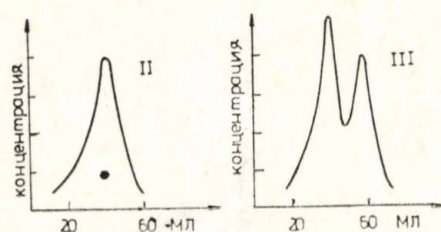


Рис. 1. — Кривые ГПХ полимеров II и III.

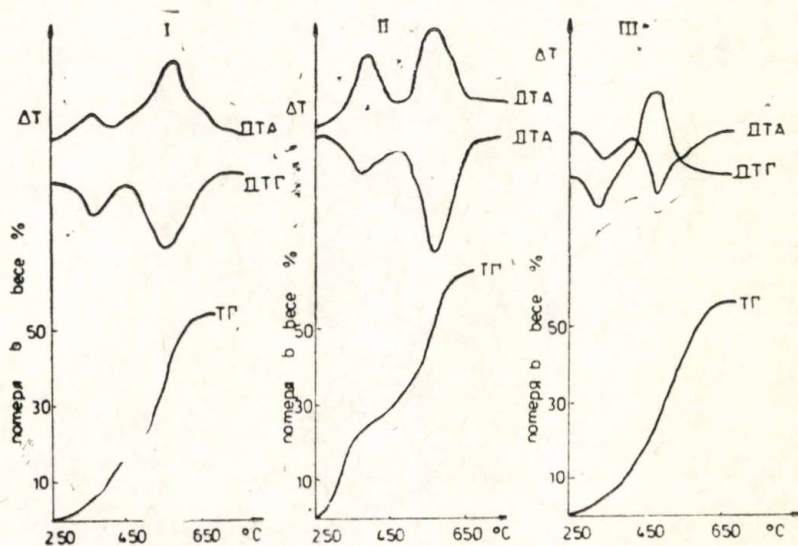


Рис. 2. — Кривые ДТА и ТГА полимеров I, II и III.

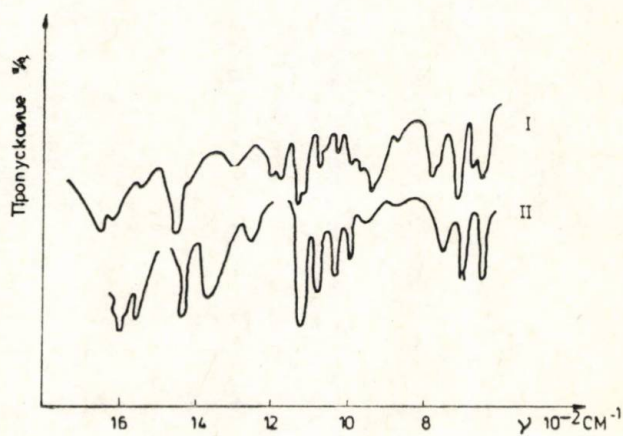


Рис. 3. — ИК - спектры полимеров I и II.



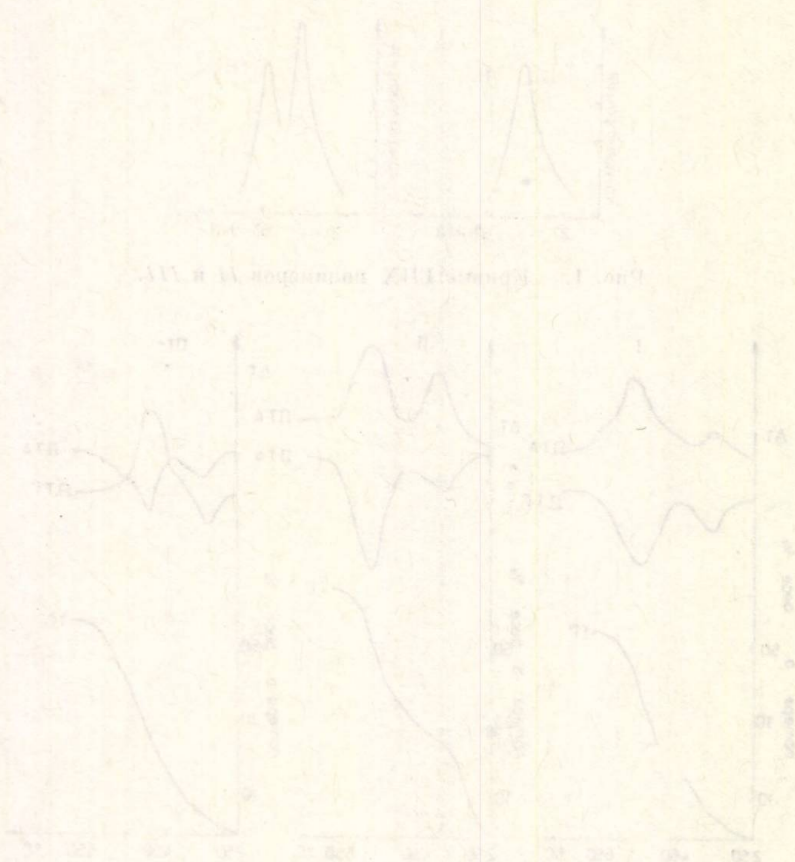


Fig. 1. Current-time curves for the reaction of the reagent with the substrate.

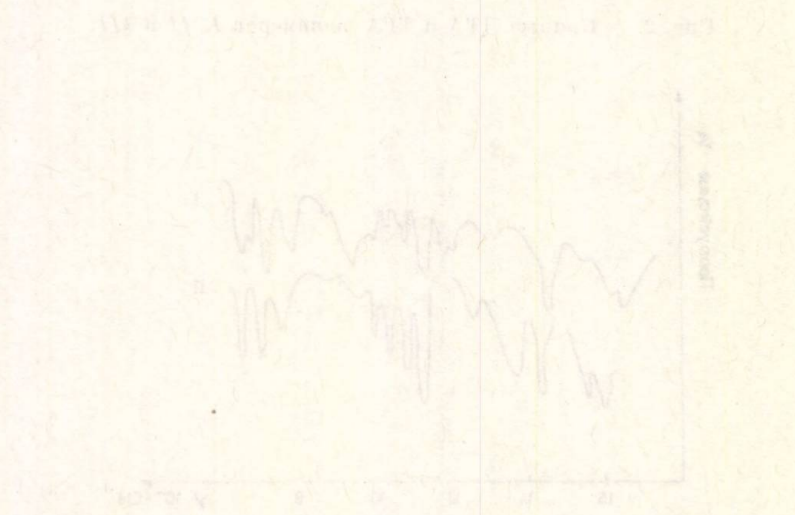


Fig. 2. Voltage-time curves for the reaction of the reagent with the substrate.

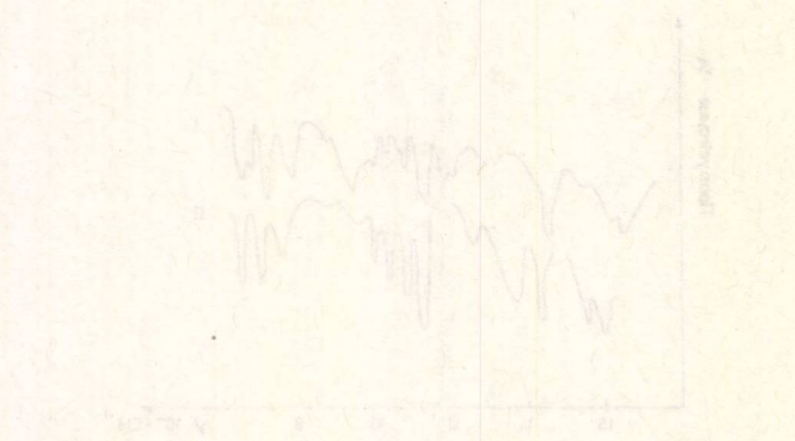


Fig. 3. Voltage-time curves for the reaction of the reagent with the substrate.

Термогравиметрический и дифференциальный термические анализы этих полимеров (скорость нагревания  $10^{\circ}\text{C}/\text{мин.}$ ) показали (рис. 2) что начало разложения наблюдается при  $250^{\circ}\dots 405^{\circ}\text{C}$ . Разложение полимеров сопровождается энергичным выделением тепла (острый экзотермический пик на кривой ДТА).

Анализируя полученные результаты, можно сказать что полимер III является несколько более термостойким, чем I и II (табл. 2).

Деструкция полимеров происходит с отщеплением органических радикалов : остаток отвечает формуле  $\text{ThO}_2 \cdot \text{P}_2\text{O}_5$ .

Таблица 2

*Характерные температуры термического разложения координационных полимеров*

| Поли-<br>мер | Температуры, $^{\circ}\text{C}$ |                          |                                |     |
|--------------|---------------------------------|--------------------------|--------------------------------|-----|
|              | Начало<br>разложения            | Прекашения<br>разложения | Соответствующие потерям в весе |     |
|              |                                 |                          | 10%                            | 25% |
| I            | 260                             | 780                      | 380                            | 435 |
| II           | 300                             | 760                      | 430                            | 495 |
| III          | 380                             | 790                      | 550                            | 620 |

Исследованные координационные полимеры обладают более высокой термостойкостью, чем соединения из которых они получены и это подтверждает факт образования полимеров мостикового типа с более устойчивыми хелатными циклами. На всех стадиях порядок реакций и энергию активаций разложения определяли по методу из [14]. На всех этапах разложения порядок реакций близок к единице (табл. 3).

Таблица 3

*Значения порядка реакции и эффективной энергии активации термического разложения полимеров I, II, III*

| Полимер | Порядок реакции |           | $E_{\text{эф.}}$ , [кДж/мол] |           |
|---------|-----------------|-----------|------------------------------|-----------|
|         | Стадия I        | Стадия II | Стадия I                     | Стадия II |
| I       | 0,78            | 0,86      | 75,9                         | 88,8      |
| II      | 0,8             | 0,9       | 78,8                         | 89,8      |
| III     | 0,86            | 0,93      | 80,1                         | 90,7      |

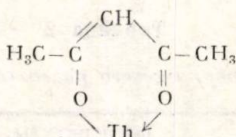
Для более точной характеристики полученных продуктов были записаны их ИК-спектры. Наиболее удобной областью спектра для количественного определения содержания радикалов дифенилфосфиновой кислоты является область  $700\dots 900$  и  $1\,100\dots 1\,200\text{ см}^{-1}$ . Полосы в области



700... 900  $\text{cm}^{-1}$  обусловлены неплоскими колебаниями ароматических групп фенильного ядра : они узки и интенсивны.

Характерные полосы поглощения связи  $\text{P}-\text{O}$  не изменяются в полимерах по сравнению с соответствующими полосами дифенилфосфиновой кислоты, но изменяются полосы поглощения группировок  $\text{PO}_2$  (рис.3).

При образовании связей  $\text{P} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{Th}$  (из радикала кислот) и



полосы поглощения, соответствующие колебаниям группировок  $\text{P}=\text{O}$  и  $\text{C}=\text{O}$  (рис. 3) изменяются из-за удлинения связей  $\text{P}=\text{O}$  и  $\text{C}=\text{O}$ . Эти колебательные частоты у полимеров меньше частот для соответствующей свободной кислоты и ацетилаcetона [16]. Группировка  $\text{P}=\text{O}$  для дифенилфосфиновой кислоты имеет характерные полосы поглощения в области 1150... 1180  $\text{cm}^{-1}$ .

Обозначая через  $\nu$  частоту характерного колебания соответствующих группировок  $\text{P}=\text{O}$  в свободной кислоте а через  $\nu'$  частоту тех же самых группировок в полимерах, по уравнению  $\Delta\nu = (\nu - \nu')/\nu \times 100$  можно найти изменение колебательной частоты группировок, которые определяют образование координационных связей, а именно : для полимера I,  $\Delta\nu = 2,4$ ; для II,  $\Delta\nu = 2,8$  и для III,  $\Delta\nu = 2,9\%$ .

Координационный полимер II обладает полупроводниковыми свойствами в области температур 20°...200°C. Изменения удельной электропроводности этого полимера показали, что она существенно зависит от температуры, подчиняясь закону  $\sigma = \exp(E/2kT)$ . Полимер II имеет энергию активаций проводимости 0,68 эв и удельную электропроводность при 100°C равную  $8 \cdot 10^{-12} \Omega \text{ cm}^{-1}$ .

### 3. Дискуссия результатов

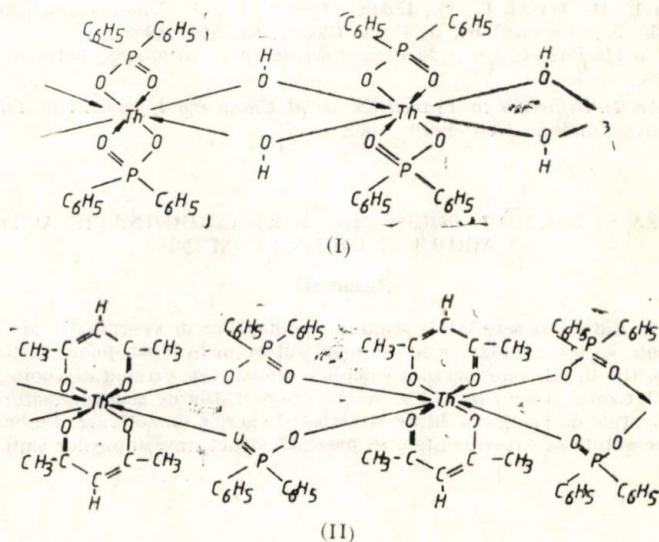
Из экспериментальных результатов следует, что на каждый ион  $\text{Th}^{4+}$  в полимерах I приходятся две группы  $\text{OH}$  и два остатка дифенилфосфиновой кислоты. Так, как эти радикалы играют роль бидентатных лигандов, ионы  $\text{Th}^{4+}$  могут осуществлять устойчивое координационное число восемь, характерное для этого иона во многих комплексах [10], [11], [15], [16]. На каждый ион  $\text{Th}^{4+}$  в полимере II приходятся две ацетилацетонатные группы и два остатка дифенилфосфиновой кислоты, для III — на каждый ион  $\text{Th}^{4+}$  приходятся четыре остатка дифенилфосфиновой кислоты. Эти радикалы играют роль бидентатных лигандов через посредство атомов кислорода что доказывают ИК-спектры полимеров II и III. В ацетилацетонате  $\text{Th(IV)}$  и во многих комплексах  $\text{Th}^{4+}$  этот ион имеет координа-



ционное число восемь [10], [15], [16]. Из ИК-спектров полимеров I, II и III следует, что радикалы дифенилфосфиновой кислоты, OH и ацетил-ацетона, связаны с ионами  $\text{Th}^{4+}$  посредством координирования, как и в координационных соединениях, где центральный ион  $\text{Th}^{4+}$  имеет координационное число восемь.

В соответствии с теорией поля лигандов [15], [16] образование координационных полимеров происходит при формировании молекулярных орбиталей (МО) между ионами  $\text{Th}^{4+}$  и радикалами дифенилфосфиновой кислоты, OH и ацетилацетона. При образовании МО от ионов  $\text{Th}^{4+}$  участвуют орбитали  $6d$ ,  $7s$  и  $7p$ ; от лигандов атомы кислорода — 16 электронов, которые располагаются на связывающих орбиталях.

Внешние орбитали  $5$  и  $7p$  центрального иона  $\text{Th}^{4+}$  взаимодействуют и лигандами сильно, а экранированные и внутренние орбитали  $4$  — слабо. На основании этих заключений можно установить возможную схему образования МО исследованных координационных полимеров с додекаэдрической структурой:



#### 4. Выводы

В работах [10], [15], [16] доказана структура координационных полимеров  $\text{Th}^{4+}$  с координационным числом восемь (с додекаэдрической структурной единицей). На основе экспериментальных результатов и литературных данных, мы так же предлагаем структуру этих полимеров с додекаэдрической структурной единицей (с координационным числом восемь для центрального атома иона  $\text{Th}^{4+}$ ).

Поступило с 15 февраля 1989 г.

Ясский политехнический институт,  
Кафедра неорганический и  
аналитический химии



## L I T E R A T U R A

1. Blok B. P., Simkin J., Ocane L. R., J. Amer. Chem. Soc. **84**, 1749 (1962).
2. Blok B. P., Rose L., Schuman C. W., Roth E., J. Amer. Chem. Soc., **84**, 3200 (1962).
3. Crescenzi V., Giancotti V., Ripemoti A., J. Amer. Chem. Soc., **87**, 391 (1965).
4. \* \* \* Успехи в области синтеза элементоорганических полимеров. Изд. Наука, Москва, 1966, 59.
5. К'оршак В. В., Крукровский С. П., Жун-Хан Ван, Локшин Б. В., Высокомолек. соедин., **В 9**, 628 (1967).
6. Коршак В. В., Крукровский С. П., Жун-Хан Ван, Высокомолек. соедин., **В 9**, 583 (1967).
7. Roșca I., Bul. Inst. polit. Iași, **16** (20), 3-4, 15 (1970).
8. Roșca I., Bul. Inst. polit. Iași, **17** (21), 3-4, 21 (1971).
9. Roșca I., *Compuși termostabili ai acetilacetonafilor de Cr(III), Mn(II), Fe(III), Cr(II), Ni(II),  $UO_2^{2+}$  cu acizi și tioacizi dialchilfosfinici și difenilfosfinici*. Докт. дисс., Полвт. инст., г. Яссы, 1975.
10. Golgoțiu T., Roșca I., Macromolecul. Chem., **59**, 160 (1972).
11. Голгоцю Т., Рошка И., Высокомолек. соедин., **А 9**, 2086 (1973).
12. Kosolapoff G. M., J. Amer. Chem. Soc., **64**, 2982 (1942).
13. Freedman L. D., Doak G. D., Edmisten J. R., J. Organ. Chem., **26**, 284 (1961).
14. Freeman E. S., Carroll B., J. Phys. Chem., **62**, 394 (1958).
15. Lewis J., Wilkins C. R., *Modern Coordination Chemistry*. Intersci. Publ., New York, 1964.
16. Orgel L. *An Introduction to Transition Metal Chemistry Ligand Field Theory*. Intersci. Publ., London—New York, 1962.

# SINTEZA ȘI STUDIUL POLIMERILOR DE COORDINAȚIE AI Th(IV) ȘI ACIDULUI DIFENILFOSFINIC

(Rezumat)

Se prezintă sinteza și rezultatele studiului polimerilor de coordinație ai Th(IV) și acidului difenilfosfinic ca o continuare a preocupării autorului în acest domeniu. S-au înregistrat spectrele de absorbție în IR, s-au efectuat calcule termocinetice privind descompunerea termică a polimerilor sintetizați și s-au pus în evidență proprietățile de semiconductori prin măsurările experimentale de conductibilitate electrică și energie de activare. Pe baza datelor din literatura de specialitate și experimentale se prezintă structura compușilor sintetizați.

## SORPTION AND SEPARATION OF SOME METAL IONS BY CHELATING SULFONATED AGENT-LOADED ION EXCHANGERS

BY

ANIȘOARA BOLD, DOINA BEJAN, DOINA BÎLBĂ and LAVINIA TOFAN

### 1. Introduction

One of the most important and modern method for separation and concentration of the element traces in order to be then analysed is the sorption by chelating resins. The rapid and efficient recovery of the microelements from large volumes of solution with complex saline composition is assured by the high selectivity of chelate sorbents, selectivity due to both nature of the chelating groups bonded on polymer matrix and the sorption conditions, namely acidity, temperature, masking compounds, etc.

The chelating group ion exchangers obtained synthetically, are well known and employed in the analytical practice [1], [2], but they have a series of disadvantages such as: special methods of synthesis, high cost, difficult regeneration and unsatisfactory kinetic characteristics.

A simple way, of great interest in the last time, for obtention of some modified ion exchangers, with complexing properties and high selectivity, is sorption of some chelating organic reagents on usual ion exchangers [3].

Utilisation of the chelating agent-loaded ion exchangers for preconcentration, selective separation and determination of some metal ions involves that the mechanism and retention conditions of organic reagents and complexes of the elements as well, as kinetics of sorption—desorption to be known [4]...[13].

The purpose of the present work is to obtain some ion exchangers loaded with 5-sulphosalicylic acid (SSA), starting from the anion exchangers Dowex 2x4 and Vionit AT-14 and their utilization for concentration and separation of Fe(III), Cu(II) and Zn(II) from aqueous solutions.

Selection of the SSA as modifier agent was determined by the fact that it contains two groups able to interact with other compounds, namely the sulphonic groups ( $-\text{SO}_3^-$ ) for bonding with the anion exchanger and the o-hydroxycarboxyl groups to react selectively with a series of elements ( $\text{p}K_2(-\text{COOH})=2.67$ ;  $\text{p}K_3(-\text{OH})=11.74$ ).

### 2. Experimental

For preparation of the chelating agent-loaded resins we used the chloride form of a strongly basic anion exchanger Dowex 2x4, gel, with the functional group  $-\text{CH}_2\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$  and batch exchange capacity of 3.0